POTENTIAL TOXICITY OF SILICON SOLAR PHOTOVOLTAIC COMPONENTS

By

Brianna Tavolacci

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Environmental Engineering – Master of Science

2024

ABSTRACT

In 2023, photovoltaic (PV) solar modules provided over 170 GW of green energy to the U.S. Currently, there is no mandatory recycling of PV waste in the U.S. and most PV modules are landfilled rather than recycled. Previous work on PV toxicity focused on metal and considered the full module. To plan for large volumes of PV waste that require management, we evaluated the potential ecotoxicity of various module components. The project was separated into two tasks: 1) acute toxicity of solar components under batch leaching conditions and 2) the design of a column landfill study. We tested three crystalline silicon modules by separating them into three components of waste: the powdered cell and glass area, encapsulation and back sheet polymers, and junction box and cables. Bioassays classified the aquatic acute ecotoxicity of each component with the half-maximal effective concentration (EC50) to crustacea, *Daphnia magna*, in which leachates were considered acutely toxic at concentrations of less than 10%.

Two of the tested module's powder and encapsulation and back sheet leachates showed little hazard to the environment with either no impact on daphnids or projected EC50s over 120%. The third module did have significant ecotoxicity with EC50s less than 5%. Each module's junction box and cable leachates had observable effects on daphnids, but only one had a significant EC50 of less than 10%. The metal and microplastic content of each leachate was evaluated to characterize potential sources of toxicity. Of the 22 elements tested, few were of concern. Silver and aluminum leached at high concentrations exceeding literature EC50 values, so toxicity was primarily contributed to these metals. Spectroscopy analysis only showed a presence of plastics in junction box and cable leachates, with peaks characteristic of polypropylene and polyethylene. Therefore, only metals were of potential concern for powder, encapsulation, and back sheet components, while the junction box and cables may release small metal concentrations and some plastics. Overall, two modules showed little to no risk to the aquatic environment, but the significant toxicity of the third emphasized the need for careful classification and disposal of all module materials. This work verified previous claims that semiconductor metals were of primary concern in PV waste, allowing for proper classification of disposal needs. The ecotoxicity of select leachates showed the increasing need for PV recycling. Future work should expand on microplastic degradation in long-term studies for greater understanding of potential release.

ACKNOWLEDGEMENTS

I owe great thanks to my advisor Dr. Annick Anctil and mentor Dr. Preeti Nain for their knowledge and guidance throughout my work. I could not of achieved my goals of study without their resourceful knowledge in the solar photovoltaic sphere or teachings on technical writing and laboratory skills. In addition, I contribute this work to my incredibly supportive research team, Dr. Angela Farina, Francis Hanna, Luyao Yuan, Jaewon Han, Chenyang Deng, Andreana Roxas, and Mallika Kothari, as well as undergraduate assistants Om Nair and Micheal Wholihan, who all gave valuable advice and assistance in my experiments. Great thanks to my committee members, Dr. Syed Hashsham and Dr. Kaisen Lin, for their expertise and as models for passionate research. Also, thank you to those at the MSU Civil Infrastructure Laboratory, technician Brian Getzel, Dr. Bora Cetin, Mohamad Yaman Fares, and Mehdi Bulduk, who all gave ample time and resources to make the column study discussed possible.

Lastly, my extreme gratitude to my family and friends, who gave me the strength and will to push through every obstacle. They knew I had high goals from a young age, but without their support it simply would not have been possible. Mostly, my amazing fiancé Jack, who never heard the end of my passionate rants on sustainability and protecting the environment. He was my rock throughout every moment of this experience.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS v

Chapter 1: Introduction 1

Chapter 2: c-Si Hazard and Toxicity Literature Review 3
- 2.1 Lifetime Hazards of c-Si Modules 3
- 2.2 Toxicity Testing Methodologies 4
- 2.3 Limitations and Gaps in Knowledge 10

Chapter 3: Aquatic Toxicity of c-Si Components to *Daphnia Magna* 12
- 3.1 Background 12
- 3.2 Methodology 12
- 3.3 Results and Discussion 16
- 3.4 Final Assessment and Conclusions 25

Chapter 4: Column Study Design and Construction for Partially Recycled c-Si Waste 28
- 4.1 Simulated landfills in Literature 28
- 4.2 Column Design and Waste Scenario Methodology 31
- 4.3 Experimental Setup 35

Chapter 5: Conclusion 37

BIBLIOGRAPHY 39

LIST OF ABBREVIATIONS

Ag	Silver
Al	Aluminum
ANOVA	Analysis of Variance
As	Arsenic
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared
Ba	Barium
c-Si	Crystalline Silicon
C-H	Hydrocarbon
$CaSO_4 \cdot 2H_2O$	Calcium Sulfate Dihydrate
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
EC50	Half-Maximal Effective Concentration
EN	Encapsulation
EOL	End-of-Life
ETFE	Ethylene Tetrafluoroethylene
Fe	Iron
HCl	Hydrochloric Acid
HDPE	High-Definition Polyethylene
Hg	Mercury
HNO_3	Nitric Acid
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
JBC	Junction Box and Cable
KCl	Potassium Chloride
$MgSO_4$	Magnesium Sulfate
Mn	Manganese
Mo	Molybdenum
$NaHCO_3$	Sodium Bicarbonate

NaOH	Sodium Hydroxide
Ni	Nickel
NREL	National Renewable Energy Laboratory
MSW	Municipal Solid Waste
Pb	Lead
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PV	Photovoltaic
RCRA	Resource Conservation and Recovery Act
Sb	Antimony
Sn	Selenium
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
Ti	Titanium
Te	Tellurium
Tl	Thallium
USEPA	United States Environmental Protection Agency
V	Vanadium
W	Tungsten
WET	Waste Extraction Test
Zn	Zinc

Chapter 1: Introduction

As of 2023, the photovoltaic (PV) solar fleet in the U.S. reached 177 GW of power and is expected to quadruple by 2034 (Davis et al., 2024). The growing PV industry was popularized for its affordable energy production and reduction of emissions in the energy sector. However, increased production also instigated an increasing waste stream at the modules' end-of-life (EOL). Due to an average degradation rate of 0.5-0.8% annually, modules had an expected warrantied life of 25 years prior to disposal (Deline et al., 2021). Based on PV lifetimes, global PV waste was projected to reach up to 160 million metric tons by 2050 (Mirletz et al., 2023). This substantial sum requires a system of waste management practices. For disposal, survey data approximated that only 10% of modules were recycled in the U.S., while the remaining 90% were sent to landfills (Curtis et al., 2021). The survey reported that the recycling rate was inhibited by a lack of widespread transportation, little storage and recycling facility infrastructure, a high cost of procedures as compared to return on investment, and inconsistencies in regulation requirements by jurisdiction. The series of recycling complications lead to landfill disposal in municipal locations, causing concern for potential exposure of contaminants to the environment.

To plan for potential exposure, the type of incoming waste must be considered. As of 2023, 70% of PV installations were crystalline silicon (c-Si) modules (U.S. Energy Information Administration, 2024) and therefore are of primary concern for landfill leaching. C-Si modules are comprised of glass (76%), polymers (10%), aluminum (Al) (8%), and silicon (Si) (5%), with standard structure shown in Figure 1. Metal connectors make up the remaining 1% with copper (Cu), silver (Ag), and lead (Pb) (Dominish et al., 2019). While the modules largely consist of glass, heavy metals could have adverse health effects at low concentrations and must be studied. Pb was of particular concern, as there is no known threshold in which health is not adversely affected (Sanborn et al., 2002). In addition, release of microplastics may also occur from polymers used in encapsulation, back sheets, junction boxes, and cables. If leaching of these materials occurred, the liquid could become environmentally toxic and require treatment prior to exposure. With potential for environmental exposure of leachates from c-Si PV waste, the ecotoxicity of waste must be evaluated.

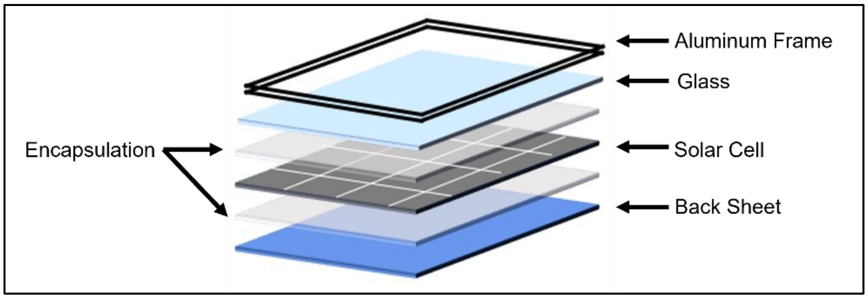

Figure 1. Standard structure of c-Si module layers including the aluminum frame, glass, encapsulation polymer, solar cells, and back sheet polymer

The following work investigated the ecotoxicity of c-Si module components through batch leaching procedures and aquatic bioassays. Crustacea, *Daphnia magna*, were used to estimate the impact of waste components on the aquatic environment. In an expansion of batch leaching, construction of a lab scale landfill column was used to understand the leaching capacity from municipal landfills to the environment. The objectives of this work are therefore as follows:

- Review existing literature discussing the hazards of c-Si modules and methodologies in which the modules were tested for toxicity (Chapter 2).
- Experimentally determine the acute toxicity of c-Si waste to *Daphnia Magna* and evaluate metal and microplastic leaching as sources of ecotoxicity (Chapter 3).
- Design and construct a system capable of experimentally testing the leachability of c-Si waste in a lab scale landfill column (Chapter 4).

Chapter 2: c-Si Hazard and Toxicity Literature Review

2.1 Lifetime Hazards of c-Si Modules

The full life cycle of a c-Si module includes raw material acquisition, material processing, manufacturing, use, decommissioning, then recycling or disposal (Kiger, 2016). Previous literature discusses the economic, environmental, and human impacts of production and manufacturing, use, recycling, and disposal. While there are ample life cycle assessment publications at various stages of c-Si lifetimes, including recycling processes and electricity consumption needs, this literature review will focus on the impacts of hazardous materials and disposal.

During production and manufacturing, hazardous materials may be emitted. Silica dust, silanes, diborane, phosphine, and various solvents could all affect human health depending on the concentration, frequency and length of exposures, receptor absorption rates, and individual sensitivities (Dubey et al., 2013). The waste left over from extraction and production could also contribute to environmental issues. Zinc in support structures could cause aquatic ecotoxicity if leaked into soil and accidental emissions of inflammable gases silane and phosphine are highly toxic (Aguado-Monsonet, 1998). Depending on the energy mix used in module production, global warming related emissions may also be of concern, but were reduced by 50% or more when recycled modules were utilized (Dubey et al., 2013). In addition, advancements in safety protocols and employee training effectively reduced the risks to human health and environmental pollution during production and manufacturing stages (Adekanmbi et al., 2024). After manufacturing, use-phase risks must be assessed.

The use-phase of c-Si technologies maintained little hazard to human health or the environment. The heavy metals of concern in c-Si modules, such as Pb, were stored within the inner cell layer for connector materials. Due to the strong bond encapsulant polymers provide, the outer glass and back sheet layers protect the inner cells and prevent leaching upon installation sites (Nain & Kumar, 2020a). Therefore, adverse impacts only occur when module breakages occur. According to the National Renewable Energy Laboratory (NREL), in installations between 2000 and 2015, the median annual failure rate was only 5 out 10,000 modules (*Researchers at NREL Find Fewer Failures of PV Panels and Different Degradation Modes in Systems Installed after 2000*, 2017). In a study utilizing fate and transport modelling to understand the transport of Pb from c-Si modules to soil and groundwater after field breakage, utility scale installations had the highest exposure concentration at 0.000001 mg/L (Sinha et al., 2019). The estimated concentration was also based on the assumptions that the breakage remained undetected for a full year and all rainwater contacted the broken module, which are highly unlikely realistic conditions. In summary, there was little risk of exposure during the average use of PV modules. However, PV disposal may be of higher concern.

Environmental toxicity impacts from PV modules at EOL depended on the disposal route, as it affected the possibility of exposure. PV modules may be recycled or sent to municipal or hazardous waste landfills. In a survey of PV manufacturers, 97% of respondents considered recycling a necessity, but only 24% were involved in any reuse or recycling practices (Nain & Kumar, 2020c). So, despite a widespread importance of recycling, landfill disposal remained more common due to a lack of regulations or incentives to recycle. Typically, non-hazardous dumping was the cheapest form of disposal. In 1997, it costed less than $100 per ton of garbage, but PV recycling costed $300-700 per ton (Eberspacher & Fthenakis, 1997). Modernly, recycling can cost up to $45 per module, whereas municipal or hazardous landfills can cost less than $1 and $5 respectively per module (Curtis et al., 2021). Regulations in the U.S., the Resource Conservation and Recovery Act (RCRA) govern hazardous and non-hazardous solid waste but do not currently classify solar PV waste (Part 261 - Identification and Listing of Hazardous Waste, 1976). The cost imbalance between recycling and landfill disposal, as well as a lack of universal regulations, led to concern for potential environmental toxicity impacts from exposure to PV waste landfill leachates. The remainder of the literature review focuses on the toxicity at EOL.

2.2 Toxicity Testing Methodologies

Multiple methodologies are used in literature to estimate the toxicity of c-Si modules at their EOL. Landfill leachate potentials were typically determined by the USEPA Toxicity Characteristic Leaching Procedure (TCLP) and the California Waste Extraction Test (WET), as well as some variations on protocol. Less commonly, some researchers expanded on TCLP and WET results to investigate the long-term dissolution of c-Si metals, while others used bioassays for estimates of environmental impact.

2.2.1 TCLP, WET, and Leaching Test Variations

The TCLP and WET tests were designed to estimate the mobility of analytes in waste to classify it as hazardous or non-hazardous (California Waste Extraction Test, 1985; U.S. Environmental Protection Agency, 1992). Both procedures modelled the environmental conditions of a landfill by reducing the waste sample size, exposing it to an acidic solution, and using end over end agitation. However, the tests have different parameters for extraction (Table 1). The WET had a more aggressive procedure than the TCLP with a lower dilution ratio, longer extraction time, and smaller sample size.

Table 1. TCLP and WET test criteria

Parameter	TCLP	WET
Solid to liquid dilution ratio	1:20	1:10
Fluid extractant	Glacial Acetic Acid & Sodium Hydroxide	Sodium Citrate
Extraction time	18 h	48 h
pH	4.93 ± 0.05	5.0 ± 0.1
Sample size	9.5 mm	2 mm

In the past decade, multiple researchers utilized the TCLP and WET procedures to investigate the toxicity of c-Si modules. Yet, despite the use of the same test procedure, the results from each publication varied greatly, as shown in Table 2. For example, of researchers using the TCLP, one group found only 3.39 mg/L leached, while another found 34.9 mg/L from c-Si modules (Collins & Anctil, 2017; Krishnamurthy, 2017). WET results for Pb also varied between 1.015 mg/L and 32.4 mg/L (Brown et al., 2018; Collins & Anctil, 2017). Even within the same publication, Brown analyzed five different c-Si modules and found Pb to range from 0.7 mg/L to 18 mg/L in TCLP testing (Brown et al., 2018). The wide variation in results is critical, as the RCRA limit for Pb is 5 mg/L. Therefore, c-Si waste could not be easily classified as hazardous or non-hazardous based on the literature results. An analysis of the variability was then required.

Table 2. Available c-Si metal leaching data (mg/L) from literature with the testing methodology used and the number of c-Si modules tested

	Metal (mg/L)																	
Leaching Method	Ag	Al	As	Ba	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Sn	Te	Zn	Num. Modules Tested	Reference
TCLP												11					1	(Sinha & Wade, 2015)
Pure Water	0.694	1.321		0.618	0.023	0.011	0.038			0.012	0.042	61.375	20.1	0.661	0.009	0.142	26	(Tammaro et al., 2016)
TCLP		3.72					1.23	0.21				34.9					2	(Collins & Anctil, 2017)
WET		3.32					9.81	1.18				32.4						
TCLP												3.39					1	(Krishnamurthy, 2017)
TCLP				0.1					0.015		0.025	17.22				0.105	5	(Brown et al., 2018)
WET				0.035		0.03					0.005	1.015				0.07		
TCLP	0.002			0.3		0.05						6.1					1	(Bang et al., 2018)
TCLP	0.004	0.815			0.0002	0.0006	0.089			0.003		9.35				0.265	1	(Sharma et al., 2021)
SPLP	0.002	0.122			0.0002	0.0009	0.079			0.003		1.39				0.138		
Static pH=3	0.003	0.436			0.0002	0.029	0.027			0.007		6.44				0.202		
Static pH=7	0.001	0.226				0.0002	0.02					0.082				0.176		
Static pH=9	0.003	0.378			0.0001		0.009			0.003		0.978				0.008		
TCLP		81.321	0.228		0.338		28.588				4.962	5.682					2	(Panthi et al., 2021)
TCLP				0.01								20.2				0.4	2	(Kilgo et al., 2022)

The TamizhMani group tested the variability of TCLP results by using multiple strategies for sample reduction (Krishnamurthy, 2017; Leslie, 2018; Tamizhmani et al., 2019). The team used five different removal methods to collect samples, including a diamond drilling core machine, strip cuts with a diamond cutting wheel, cell cuts with a diamond cutting wheel, a hybrid strip cut and core, and a water jet cutter. After samples were collected with each methodology, they were analyzed with image processing techniques to determine the remaining glass coverage. The water jet cut samples remained the most intact and coring maintained consistency, but others lost coverage and had low sample size accuracy. When sent to a TCLP laboratory, Pb concentrations in the samples ranged from less than 1 a.u. to almost 10 a.u., despite testing the same module (Leslie, 2018). The group discusses this variability as due to differing glass coverage, as well as possible bias in sampling location of the module. The c-Si cells do not universally cover the cell layer, as connector strips separate cells. The TCLP laboratory may have inadvertently taken samples from a connector strip rather than cell area, causing variation in the results. The team verified that the way samples were collected could significantly alter the TCLP results and hazard classification.

Other researchers also investigated the impact of glass coverage and particle sizing. Sharma et al. tested modules both with and without encapsulation and glass (Sharma et al., 2021). The team used the TCLP test, as well as the EPA Synthetic Precipitation Leaching Procedure (SPLP) and a pH static leaching procedure to test 60 silicon wafers. The SPLP differs from the TCLP in that it modelled precipitation leaching rather than landfill leaching. The pH procedure used solutions of 3, 7, and 10 pH by varying mixtures of deionized water, nitric acid, and sodium hydroxide. Overall, each test resulted in a higher leaching rate from the samples without glass and encapsulation intact. Of the three test procedures, the TCLP observed the highest concentrations, with Pb leaching between 8.7 to 9.3 mg/L. The SPLP ranged from 1.1 to 1.4 mg/L and the pH static tests 0.07 to 6.7 mg/L. Another team, Song et al., compared four sample particle sizes to investigate how the size may impact the leaching of silver when exposed to nitric acid (Song et al., 2023). The researchers confirmed that the smaller the sample size, the higher the amount of silver (Ag) leached. These publications confirm that intact modules with protective layers limit the mobility of hazardous elements, as openly exposed and heavily crushed samples were capable of leaching at higher rates.

In summary, multiple researchers focused on the Pb concentrations leached from c-Si modules (Sinha et al., 2014; Sinha & Wade, 2015). However, additional publications found Ni, Ag, Cu, and Al also leached in high concentrations under various conditions (Bang et al., 2018; Collins & Anctil, 2017; Panthi et al., 2021). The high inconsistency of leaching results may indicate that use of harsh acidic solutions and small particle sizes, such as in the TCLP and WET, were not fit to accurately determine the leaching potential of modules. The Sinha and Wade group compared the TCLP to the German and Japanese leaching procedures. They found that Pb had little to no detection in the other countries' test procedures. Whereas with the TCLP, Pb leached up to 11 mg/L (Sinha & Wade, 2015). The use of these acidic solutions and particle sizes may therefore overestimate the impact of c-Si waste and other leaching procedures should be explored.

2.2.2 Long-Term Procedures

While the TCLP and WET procedures are short-term tests meant to represent accelerated results, some researchers expanded work to include long term studies. Publications spanned from two months to one and half year long experiments (Nain & Kumar, 2020b; Nover et al., 2017, 2021; Zapf-Gottwick et al., 2015). In Zapf-Gottwick's two-month study, a c-Si module was water jet then milled into 0.2 mm pieces, then shaken in three different solutions (Zapf-Gottwick et al., 2015). The solutions mimicked different environmental scenarios, including low mineralized water at a pH of 8.4, seawater at pH 7.8, and rainwater at pH 3. Similarly to the short-term studies, Pb was of primary concern and focus. Pb concentrations peaked with a 40% increase after 10 days in the rainwater solution, then reduced slightly as the pH reached 6.1 by the end of the study. In the low mineralized water and seawater, low leaching rates were recorded as Pb was precipitated as chlorides. The study also explains the slight reduction in Pb concentration in the rainwater as due to precipitation after a pH increase over time. The publication confirmed the trend discovered in short-term studies, in that harsh acidic conditions lead to high leaching rates with results dependent on pH.

In a longer study conducted by Nain and Kumar, a pH comparison was also used (Nain & Kumar, 2020b). For a yearlong experiment, pH 4 rainwater, pH 7 groundwater, pH 10 seawater, and a municipal solid waste leachate (MSW) were used. Samples were micro-sheared into one to two cm^2 pieces then reduced to a millimeter size with a mortar-pestle and stainless-steel mixer-grinder. The team also saw the highest dissolution rates in acidic rainwater. A monocrystalline module leached Ni, Pb, Al, and Cu at 29.8%, 17.9%, 13.9%, and 12.9% respectively. A multicrystalline module leached Pb, Cu, Al, and Ni at 24.4%, 16.9%, 21.3%, and 25.9% respectively. The results increased for the first five months, then stabilized. The impact of the pH on leaching rates verified the previous work established by Zapf-Gottwick.

The longest study conducted by Nover et al. leached 5 by 5 cm^2 module pieces for 1.5 years (Nover et al., 2017, 2021). The team simulated acid rain at pH 3, groundwater at pH 7, and alkaline percolating water at pH 11. After one year, the highest leaching rate witnessed was Al at 22% in acidic solutions, followed by 1.4% of Pb and 0.1% of Cu. After the full 1.5 years, the concentrations of Al and Pb increased to 27% and 3.7%. This work verified that element dissolution is dependent on both pH and time spent in the environment.

The long-term studies discussed showed the significance of pH on potential leaching. pH was critical to the classification of c-Si waste, as it influenced the solubility of hazardous metals. It is also important to note that leaching stabilized in two of the studies but progressed in the third after a longer observational period. The studies consequently allow for a greater understanding of the variable dissolution characteristics of c-Si modules. However, the long-term studies discussed do not identify how the leachates may impact species in natural environments.

2.2.3 Bioassays

Few publications utilized bioassays to evaluate potential adverse effects of PV waste on living plants and animals (Kwak et al., 2021; Motta et al., 2016; Tammaro et al., 2016). Each publication used aquatic species to test PV leachates for negative biological impacts including mortality or mobility, decreased germination, or developmental issues.

Tammaro et al. assessed cells from 26 c-Si modules, in which an isolated cell was crushed and shaken for 24 hours at a 1:10 solid to liquid dilution ratio (Tammaro et al., 2016). Three toxicity tests were used to compare with chemical leaching data. Bacteria (*Vibrio fischeri*) were evaluated for bioluminescence reduction, algae (*Pseudokirchneriella supcapitata*) for growth inhibition, and crustacea (*Daphnia magna*) for immobility. Ecotoxicity was classified by the effective concentration (EC) causing a response, in which a 20% response (EC20) for bacteria and 50% response (EC50) for algae and crustacea were considered. However, the publication did not report the toxicity response for each of the tested species. The modules were classified as ecotoxic to the species after comparison with threshold limits reported by the Italian Institute for Environmental Protection and Research. Yet, the actual EC20 or EC50 observed was not reported. Rather, the publication reports which modules were ecotoxic, according to the thresholds, to one, two, or three of the species. Of the tested c-Si modules, more than 80% exceeded a threshold and were considered ecotoxic. This broad classification lacks clarity on the actual impact of PV leachates on the species, as it was difficult to distinguish how modules and biological impacts compared.

Another study conducted by Motta et al. also used multiple species to evaluate modules (Motta et al., 2016). Germination tests for *Cucumis sativus* and *Lens culinaris*, immobility toxicity tests with *Daphnia magna* and *Artemia salina*, developmental toxicity tests with *Paracentrotus lividus*, and cell length analysis of *Lens culinaris* were all used. Each test utilized leachate from a monocrystalline PV module with crushed glass to expose the inner semiconductor, mimicking an accidental crash. In germination testing, *Cucumis sativus* seeds germination percentage significantly decreased after exposure but *Lens culinaris* had no observable effects. Cells of *Lens culinaris* were impacted though, as they were shortened and irregularly shaped with a reduced number of nuclei. In toxicity testing, *Daphnia magna* had an increased mortality at 32% as compared to less than 10% in controls, while *Artemia salina* had no significant differences. After exposure, *Paracentrotus lividus* eggs had irregularly shaped membranes and zygotes, indicating a disruption in development. The comprehensive report of impacts on various species allowed for an assessment of the modules' effects on multiple trophic levels. However, the study lacked an analysis on the concentration of the leachate. The publication only investigated the worst-case scenario in which the species was in contact with 100% leachate. In real environmental scenarios, the leachate would be diluted with rainwater or surface waters, altering the toxicity of the solution. Therefore, an analysis of leachate concentrations was required.

Lastly, Kwak et al. used bioassay data to compare the impacts of perovskite and c-Si solar cells (Kwak et al., 2021). The study used cells cut into 1.5 by 0.8 mm pieces, then leached the samples with the TCLP test. The filtered leachate was then exposed to zebrafish and *Daphnia magna* for immobility toxicity analysis in 0% to 50% concentrations. Overall, the c-Si cells were more toxic to both species than the perovskite cells. In testing the c-Si cells, *Daphnia magna* were more sensitive to the leachates than the zebrafish at EC50's of 6.25% and 9.71% respectively. With EC50's of less than 10%, the ecotoxicity of the c-Si cells were considered significant. Upon metal analysis, Si, Pb, and Al were the most leachable elements and therefore faulted for the observed ecotoxicity. As compared with the previously conducted studies, Kwak analyzed the impact of various leachate concentrations. Although, the tested concentration responses were shown with bar graphs rather than a statistical regression. The data was then limited to the observed response without an estimation of intermediary concentrations or projection to the 100% response rate. The publication may have benefited from a statistical regression in which a dose-response survival analysis could occur.

The discussed bioassays provided a basis for the impact of c-Si waste on living species. Each publication showed that c-Si waste had the potential to adversely affect flora and fauna. Nonetheless, the limited number of sources prevented a full assessment of adverse effects that could occur. For a comprehensive analysis, multiple leachate concentrations with statistical analysis were required to understand how c-Si modules may vary in different conditions.

2.3 Limitations and Gaps in Knowledge

The toxicity methodologies used in literature have multiple limitations. Short-term leaching procedures such as the TCLP and WET were meant to standardize toxicity testing by designating the extractant fluid, pH, sample size, and solid to liquid leaching ratio. Previous research showed that sample collection methods and locations for sampling on PV modules could affect the toxicity level reflected by the TCLP and WET. The inconsistency in results for c-Si modules inhibited a full hazard assessment. Long-term procedures provided analysis of potential leaching in different environmental conditions, including seawater, groundwater, and rainwater. While the procedures indicated a strong correlation between toxicity and pH, they did not determine the impact of the tested waters to natural species. Studies that investigated the impact on living species through bioassays were sparce and did not provide full statistical regression analysis for data. Without a graphed dose-response curve, it was difficult to discern the impact of leachates on the species tested. With these limitations in mind, gaps in knowledge were recognized by identifying commonalties within the discussed literature.

Three main gaps in knowledge were established. First, previous works used comprehensive samples or isolated cell samples for a full toxicity report. In each publication, the semiconductor layer was of focus due to concern for hazardous metals. Yet, no publication verified if the semiconductor was the only source of toxicity from c-Si waste. Second, the impact of polymers and plastics within waste was ignored as a possible source of ecotoxicity. Multiple components of c-Si modules, including encapsulation, back sheets, junction boxes, and cables, were comprised of polymers but went untested. Third, few studies investigated the potential environmental toxicity of waste in the absence of harsh acidic leaching procedures for leaching scenarios outside of a landfill environment. Expanded use of bioassays would determine the actual impact of c-Si modules on ecosystem populations.

Chapter 3: Aquatic Toxicity of c-Si Components to *Daphnia Magna*

3.1 Background

The present study addressed the above-stated knowledge and data gaps by investigating the aquatic ecotoxicological impact of reduced c-Si waste components with *Daphnia Magna* bioassays. Three components were characterized for the study: the powdered cell and glass layers, the encapsulation and back sheet polymers, and the junction box and cables. This study investigated both metal and microplastic leaching from separated components to analyze all possible sources of toxicity. Mechanical recycling separation techniques were used to consistently separate materials from each module. A batch leaching procedure was used to collect leachates from each component for bioassay testing. Bioassay results were then assessed with a Probit regression analysis and compared with metal element and microplastic data.

3.2 Methodology

3.2.1 Sample Preparation

The following three c-Si modules were used for testing: Renogy mono-crystalline (Mono-Si), Renogy flexible mono-crystalline (MonoFlex-Si), and ACOPOWER multi-crystalline (Multi-Si), with detailed specifications shown in Table 3. The modules were purchased online and reflect readily available technologies. Each module was reduced and categorized into three components: the junction box and cables (hereafter, JB-C), encapsulation and back sheet polymers (EN-B), and powdered cell and glass layers (powder). A handheld circular saw was used to remove aluminum frames when applicable, and JB-Cs were manually scraped from the back sheet. The junction boxes and cables were then cut with a table saw and a wire cutter into pieces of approximately 1×1 cm^2. A water jet cutter was used to reduce the remaining module into 1-inch-wide strips for proportional sampling of all materials within the module.

Table 3. c-Si module specifications including model number, capacity, and size

Specifications	Monocrystalline (Mono-Si)	Multicrystalline (Multi-Si)	Semi-Flexible Monocrystalline (MonoFlex-Si)
Manufacturer	Renogy	ACOPOWER	Renogy
Module Number	RNG-100-D-SS	HY100-12P	RNG-100DB-H
Total weight (kg)	6.4	9.5	2.4
Voltage (V)	12	12	12
Power (W)	100	100	100

Figure 2 outlines the full sample collection procedure and is detailed as follows. The glass was manually removed from the surface of the strips by mortar and pestle, then delaminated by peeling the surface EN-B layer to expose the cell area. All material of the separated strip was ground by a planetary ball mill (Chishun Tech model PM2L) in 500 mL zirconia grinding jars with 6-, 10-, and 20-mm zirconia balls for a total ball mass of 400 g. An approximate waste-to-ball mass ratio of 1:10 was maintained, as strips ranged between 35-45 g. The strips were ground in 15-minute intervals at 450 rpm, with 10-minute breaks to prevent polymer melting, for a total grinding time of 1.5 hours. A standard No. 12 mesh sieve was used to separate the EN-B particles from the powder.

Samples were subjected to a batch leaching procedure by rotating the sample at approximately 45 rpm with a Cole-Palmer Roto-Torque Heavy Duty Rotator for a 24-hour exposure period. The samples were mixed with deionized water at a solid to liquid ratio of 1:20 in 50 mL bottles. Rotated powder and EN-B samples were allowed to settle overnight and then centrifuged at 1500×g for 10 min. The supernatant of the leached JB-C sample was collected with a pipette. Laboratory-grade HDPE containers were used throughout all stages of leaching and storage to prevent microplastic contamination from outside sources.

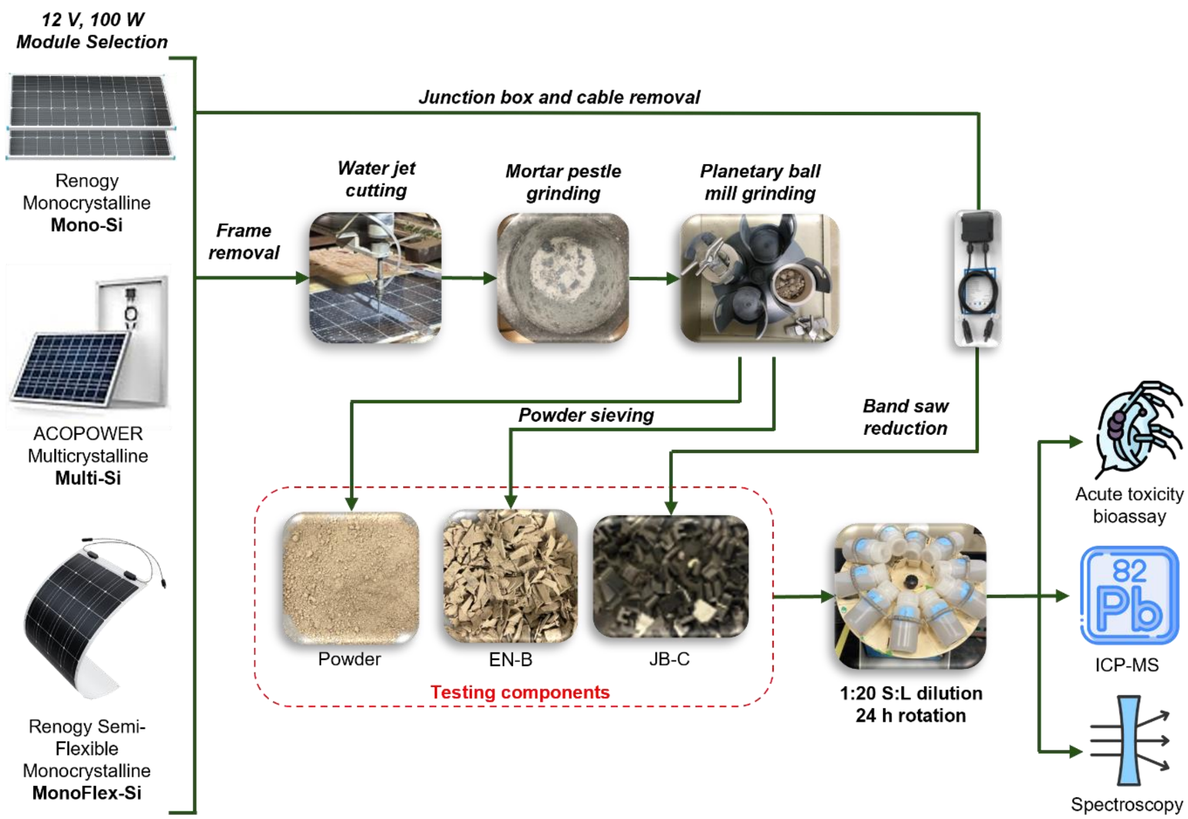

Figure 2. Summarized methodology showing the module selection, water jet cutting to ball mill grinding for powder and EN-B collection, junction box removal and JB-C sample collection, to batch leaching and testing parameters

3.2.2 Acute Toxicity Bioassay

Acute toxicity experiments were conducted to estimate the half maximal effective concentration (EC50) to planktonic crustaceans, *Daphnia Magna*. Due to their high sensitivity to environmental changes and susceptibility to toxic contamination, daphnids serve as ideal model specimen for simplistic acute toxicity testing based on immobilization (Tkaczyk et al., 2021). Experiments were performed in accordance with the U.S. EPA Procedures for Conducting *Daphnia Magna* Toxicity Bioassays (Biesinger et al., 1987). After collection, the leachate's pH was adjusted to between 6.8 to 8.5 using hydrochloric acid (HCl) or sodium hydroxide (NaOH). Each leachate was tested at a minimum of five different concentrations, with a dilution factor of 0.5 or greater. Five neonates (less than 24 hours old) were tested in each beaker, with four replicate beakers for each concentration. During testing, the daphnids were not fed, temperature was maintained at 20±2°C, and light intensity was approximately 50 FC for a 16-hour daily photoperiod, following

EPA protocol. Probit regression analysis was conducted using Minitab software to determine the EC50 of collected data.

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) designated three aquatic hazard levels to classify acute toxicity. Category 1 has principal hazard with EC50s less than 1 mg/L, Category 2 has moderate toxicity at 1-10 mg/L, and Category 3 requires some regulation with slight toxicity at 10-100 mg/L (United Nations, 2023). However, the c-Si component leachates tested were mixtures of multiple unknown materials and could not be classified based on the GHS parameters. Previously, studies testing PV or other electronic wastes used percent concentration thresholds of 1-10% to classify high toxicity (Dagan et al., 2007; Kwak et al., 2021). With similar goals in mind, the toxicity of the samples was then classified with a 10% concentration threshold to identify hazard associated with the leachate.

Adult daphnid cultures were fed 5 mL of *Raphidocelis Subcapitata* algae and 2.5 mL of YTC trout food three times a week. The cultures were maintained in reconstituted hard water (containing $NaHCO_3$, $CaSO_4•2H_2O$, $MgSO_4$, and KCl) of pH 7.6-8.5, hardness 160-180 mg/L $CaCO_3$, and alkalinity 110-120 $CaCO_3$. Water was changed every Monday, Wednesday, and Friday. Reconstituted water was used as dilution media for acute testing.

3.2.3 Material Characterization

An initial characterization was performed on each module to determine the total metal content of individual components. Solid samples of the three categorized components were digested by an adjusted EPA Method 3050B (U.S. Environmental Protection Agency, 1996), in which 10 mL of 1:1 nitric acid was refluxed with 1 g of sample, cooled, then refluxed with 5 mL concentrated nitric acid. The resulting liquid was diluted to 100 mL and filtered with 0.45 μm membrane filter paper, then read by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo Scientific ICAP Q quadrupole).

Batch leachates were tested for potential metal and microplastic contamination. For metal analysis, 50 mL were digested in triplicates using a modified EPA Method 3010A24 with 5 mL nitric acid, and the results were analyzed by ICP-MS. Since Method 3010A requires 100 mL of leachate, the ICP-MS results were doubled to reach a full reading.

For microplastic analysis, duplicates of 50 mL samples of each leachate were filtered with 0.45 μm papers, which were allowed to dry overnight. Two analytical methods were utilized to attempt to characterize plastic materials within the leachates. The dried filter sample was read in five locations within one paper quadrant with both Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy and Raman spectroscopy. The OMNIC Specta and Wiley KnowItAll databases were used to assist in the characterization of peaks for ATR-FTIR and Raman, respectively.

3.3 Results and Discussion

3.3.1 Bioassay Results

The ecotoxicity assessment of the three c-Si modules was conducted based on the EC50 immobility of *Daphnia magna*. The responses ranged from a 0% leachate control to a 100% immobility rate, tested across at least five different concentrations. The responses were represented as cumulative immobility curves and individual linearized probabilities (Figure 3).

Daphnid immobility response rates to the powdered cell and glass layers varied with the module and pH. High variations in pH decrease daphnid survival rate, mainly in highly acidic or basic environments (El-Deeb Ghazy et al., 2011). The EPA accordingly recommends an adjustment. The powder (i.e., PV cells and glass) of the Mono-Si and Multi-Si modules were highly abundant compared to other components. The two powders were therefore selected to investigate the impact of pH on ecotoxicity by testing them both with and without a pH adjustment. With the limited powder extraction for the MonoFlex-Si module, only the standard procedure with pH adjustment was conducted.

The Mono-Si and Multi-Si powders' original pH's were 11.56 and 11.55, which were adjusted to 7.62 and 7.15 with HCl. After adjustment, the Mono-Si powder had the least impact on daphnids with no response to any tested leachate concentrations. The Multi-Si module had little response at only a 10% mortality rate upon 100% leachate exposure, projecting an EC50 of 182% (Figure 2A). Without a pH adjustment, the Mono-Si and Multi-Si modules exhibited acute responses of 61% and 0.6% (Figure 2b), respectively. The increase in response suggests a correlation between pH levels and the toxicity of the tested environment. Previous research compared the leaching capacity of c-Si modules under varying pH conditions, finding that neutral pH levels reduced Pb concentrations due to precipitation as chlorides(Zapf-Gottwick et al., 2015). Additionally, group I cations, Ag^{+}, Pb^{2+}, and Hg^{2+}, produce insoluble chlorides when exposed to diluted HCl (Experiment 2-3 Qualitative Analysis of Metal Ions in Solution, n.d.). During experimental pH manipulation, precipitation of the powder leachate was observed. The combination of a neutral environment and a reaction with HCl may have stabilized the powder leachates and decreased the associated toxicity of contaminants.

The MonoFlex-Si module powder exhibited a significant impact with an EC50 of 1.3% (Figure 2A). At the lowest concentration tested (0.75%), there was a 60% immobility response, indicating no observed threshold for adverse effects. Among the powders tested, MonoFlex-Si powder showed the highest acute toxicity. Unlike the Mono-Si and Multi-Si modules, the MonoFlex-Si module uses an ethylene tetrafluoroethylene (ETFE) film instead of a thick glass layer for surface coverage. During grinding, the glass in the Mono-Si and Multi-Si modules adds substantial mass to the powder, reducing the overall proportion of the cell in the mixture. The absence of glass in the MonoFlex-Si powder likely increases the impact of the cell when the module is ground.

The leachate analysis from the EN-B test indicated a consistent trend, with the MonoFlex-Si module exhibiting the highest environmental impact and the Mono-Si module the lowest. Neither the Mono-Si nor the Multi-Si module had a significant impact on daphnids. The Mono-Si module showed no observable response, whereas the Multi-Si module had a projected EC50 of 127% (Figure 2C). In contrast, the MonoFlex-Si module resulted in an EC50 at a mere 5% leachate concentration, underscoring its elevated risk compared to the other tested modules. The EN-B results may have been affected by residual powder adhering to the surface of the polymer pieces post-sieving, thereby potentially reflecting the toxicity profile of the powder itself. In contrast to powder, Daphnids exhibited no response to the Mono-Si module and showed a comparable response to both the Multi-Si and MonoFlex-Si modules.

The ecotoxicity of JB-C leachates deviated from the previously observed trend. Among the tested modules, the Mono-Si module showed the highest ecotoxicity, followed by the Multi-Si module and, finally, the MonoFlex-Si module, with EC50 values of 9%, 27%, and 52%, respectively (Figure 2D). These observations partially correlate with the total mass of each module’s composite JB-C, which were 96.07 g for Mono-Si, 208.96 g for Multi-Si, and 185.79 g for MonoFlex-Si. The pronounced ecotoxic response rate to the Mono-Si JB-C can be attributed to its significantly lower mass. The 1:20 solid-to-liquid ratio used during batch leaching results in a higher proportion of JB-C material being leached than the other modules. However, the discrepancy in EC50 values between the similarly massed Multi-Si and MonoFlex-Si modules suggests that factors other than total mass also influence acute toxicity.

Overall, few leachates showed significant risk to daphnids. Previous assessments classified significant toxicity when the EC50 fell below 10% concentrations, as adverse effects occurred under high dilution amounts (Kwak et al., 2021). With this classification, only 4 leachates indicated risk. The powder and EN-B leachates from the MonoFlex-Si were the most significant, with EC50's of 1.3% and 5%. The Multi-Si module powder did have significance when pH went unadjusted with an EC50 of 0.6%. In standard testing conditions, neither the Mono-Si nor Multi-Si modules showed any risk to the aquatic environment. Lastly, the only JB-C leachate with significance was the Mono-Si module, which fell close to the 10% threshold at 9%.

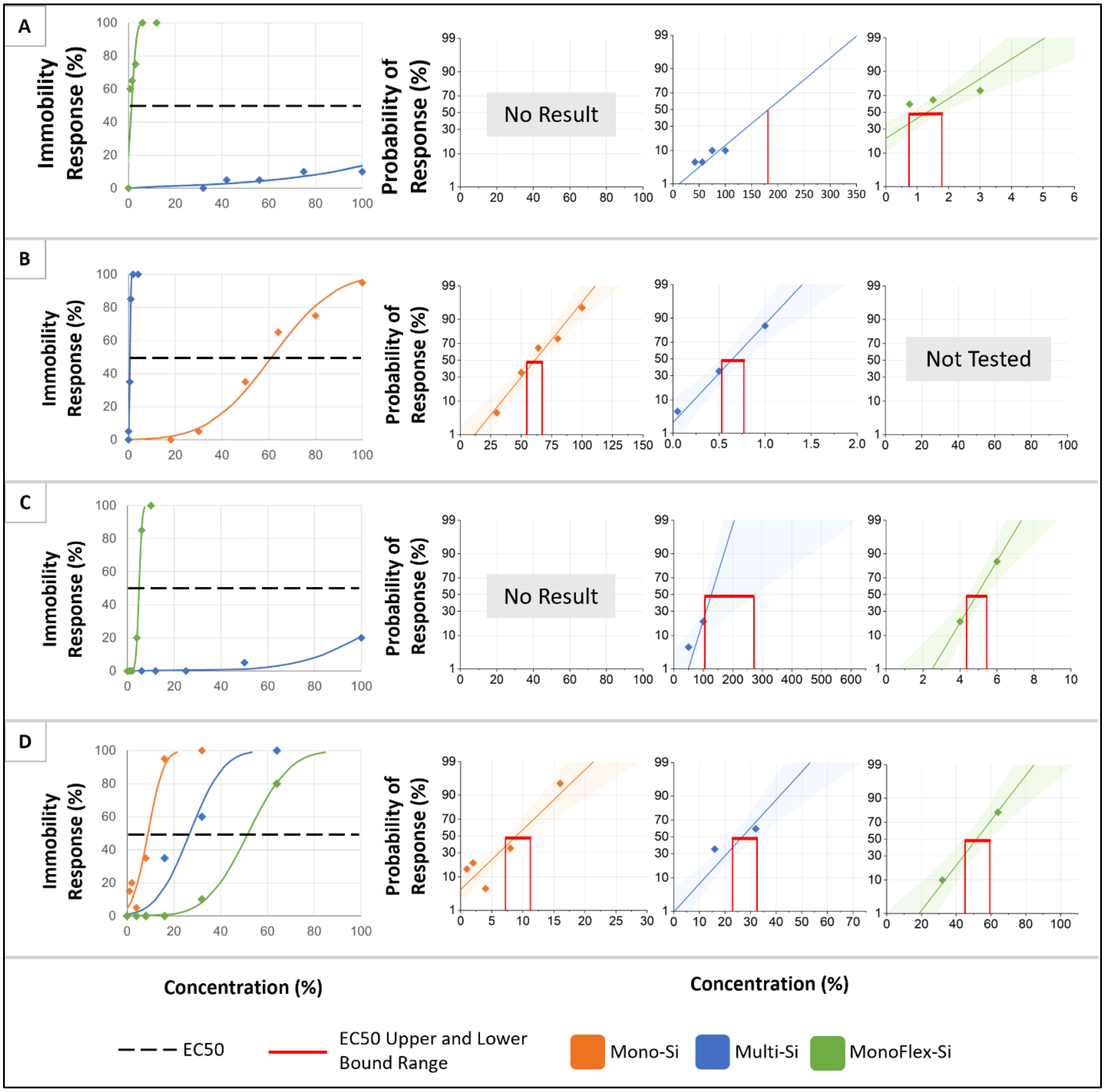

Figure 3. Composite acute toxicity results showing cumulative immobility response to leachates and individual probability curves displaying the 95% confidence interval, in which leachates are (A) powder with pH adjustment, (B) powder without pH adjustment, (C) encapsulation and back sheet, and (D) junction box and cables

3.3.2 Metal Leaching

Following up on the acute toxicity results of different components from the last section, this section thoroughly investigates the sources of observed toxicity. The toxicity of heavy metals has been well documented and should be assessed. Specifically, daphnids are known to be particularly sensitive to Pb, Cr, Hg, Cd, Co, Ni, Cu, Zn, Ag, and Tl (Fargasova, 1994; Okamoto et al., 2015). Therefore, a comprehensive elemental analysis was conducted for 22 metal elements in solar PV components (Table 4) and leachate samples (Table 5).

The leachate results were compared against the EPA's acute aquatic quality criteria (U.S. Environmental Protection Agency, n.d.) and reported EC50 values to *Daphnia Magna* in previous publications (Biesinger & Christensen, 1972; Meng et al., 2008; Oikari et al., 1992; Okamoto et al., 2015; Traudt et al., 2017; Vorobieva et al., 2020). Literature values were gathered through Google Scholar searches on daphnid acute toxicity to metal elements. Of the 22 tested metals, only four exceeded literature acute toxicity thresholds: Ag, Al, Cu, and Zn. Notably, each leachate surpassed the acute toxicity level reported in literature for Ag. Ag has high electrical and thermal conductivity and is frequently used in both modules and cables (Martinka, 2022; Zhang et al., 2022). However, Ag is highly toxic to aquatic species, as it can bind with negatively charged gills (Bianchini et al., 2002). The high concentrations observed likely contributed to the acute toxicity readings. Additionally, Al and Cu concentrations exceeded the literature values in five and four out of nine leachates, with other samples approaching thresholds. With multiple metals present at high concentrations that have known ecotoxicological impacts of daphnids, these metals plausibly caused the detected ecotoxicity.

The literature also addresses multiple synergistic effects of heavy metals (Jana & Choudhuri, 1984; Tomasik et al., 1995). During testing with daphnids, a strong synergistic relationship was observed between Ni and Zn, while a weaker synergism was noted between Mn and Co, Fe and Co, Fe and Mo, and Fe and Zn (Tomasik et al., 1995). Consequently, the lower concentrations of Ni, Zn, Mn, Co, and Fe in various leachates may significantly amplify the observed acute toxicity through these interactions.

Among the tested metals, Al and Ag concentrations were particularly high in powder and EN-B leachates. High Al concentrations in Multi-Si and MonoFlex-Si powders correlate with the acute toxicity results, with MonoFlex-Si powder exhibiting the highest Al levels and highest acute toxicity. Additionally, the Multi-Si powder showed significant toxicity when the pH was unadjusted. Al can fully precipitate as aluminum hydroxide at a pH of 6.7 to 7 (Marion & Thomas, 1946). The precipitation of high Al concentrations in the Multi-Si powder may have contributed to the difference in observed toxicity between adjusted and unadjusted pH conditions.

Silver solubility also reduces at neutral pH levels (Molleman & Hiemstra, 2017). Interestingly, Ag concentrations were higher in the EN-B leachates than the powder leachates, yet the dose-response curves for both the powder and EN-B were closely aligned. The discrepancy between the concentration and the acute toxicity results may be attributed to the reduced solubility of Ag. If the EN-B leachates were tested without pH adjustment, the toxicity results might increase, as observed with the powder. Higher Ag concentrations may remain soluble and thus have a greater impact on the acute toxicity of the EN-B leachates.

Pb concentrations should also be noted, as Pb leaching has been of primary concern in previous PV toxicity studies. Although the observed concentrations did not exceed the average literature EC50 value, several samples surpassed the EPA's recommended acute freshwater quality criteria. Specifically, all three EN-B leachates and Multi-Si powder exhibited concentrations above the EPA limit. The higher Pb concentrations in the EN-B compared to the powder can potentially be attributed to the reduction process used in the methodology. Pb soldering, known for its strong tensile properties (Plumbridge & Gagg, 2000), may have remained in larger pieces that did not sieve through during powder collection, leading to their inclusion in the EN-B mixtures.

In summation, the high toxicity of powder and EN-B leachates from the MonoFlex-Si module as compared to the Mono-Si and Multi-Si modules was likely due to the proportion of available metals in the leachate. The absence of glass in the mixture allowed for the batch leached amount to primarily comprise of semiconductor metals such as Al and Ag. Overall, the concentrations of Al strongly correlated with the powder toxicity results. The MonoFlex-Si module had the highest Al concentration and the highest acute toxicity, as well as the lowest concentration and acute toxicity in the Mono-Si module. The reduced toxicity results from the Mono-Si and Multi-Si powder leachates under a pH adjustment as compared to without was likely to a precipitation of metals at neutral pH’s.

Table 4. ICP-MS material characterization of elements as averaged from triplicate samples

		Mono			Multi			MonoFlex		
		Powder	ENB	JBC	Powder	ENB	JBC	Powder	ENB	JBC
Element (g/kg)	Ag	3699.693	5593.161	19.725	3982.643	5243.043	15.485	14838.969	11785.188	22.532
	Al	10.046	16.695	189.432	44.589	23.784	64.670	560.104	93.067	43.362
	As	0.000	0.000	0.005	0.000	0.001	0.019	0.001	0.001	0.001
	Ba	0.052	0.133	0.013	0.035	0.026	0.179	0.052	0.014	0.004
	Cd	0.0003	0.0001	0.0002	0.0003	0.0002	0.0008	0.0029	0.0002	0.0003
	Co	0.000	0.000	0.001	0.000	0.001	0.000	0.002	0.004	0.026
	Cr	0.004	0.002	0.005	0.003	0.001	0.002	0.015	0.007	0.004
	Cs	0.0002	0.0001	0.0001	0.0002	0.0001	0.0001	0.0012	0.0005	0.0001
	Cu	31.563	142.077	245.431	25.187	0.594	245.431	74.054	13.165	17.436
	Fe	0.984	0.178	0.324	0.450	0.174	0.215	2.101	0.627	0.617
	Hg	0.0002	0.0002	0.0000	0.0001	0.0001	0.0000	0.0002	0.0002	0.0000
	Mn	0.019	0.005	0.008	0.013	0.008	0.013	0.033	0.011	0.022
	Mo	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000
	Ni	0.012	0.039	0.003	0.007	0.004	0.009	0.094	0.007	2.372
	Pb	3.925	11.341	0.001	3.330	0.418	0.006	5.302	6.188	0.018
	Sb	0.144	0.006	0.004	0.063	0.125	0.030	0.058	0.064	0.012
	Sn	1.440	0.297	0.030	0.281	0.432	0.068	1.517	2.530	0.276
	Ti	0.078	0.009	0.004	0.040	0.051	0.068	0.669	0.062	0.099
	Tl	0.0000	0.0001	0.0000	0.0015	0.0018	0.0000	0.0001	0.0000	0.0001
	V	0.017	0.020	0.001	0.016	0.017	0.002	0.042	0.011	0.001
	W	0.003	0.001	0.000	0.001	0.002	0.000	0.000	0.004	0.000
	Zn	0.070	0.087	0.365	0.099	0.093	0.644	0.716	0.151	65.736

Table 5. ICP-MS elemental analysis of leachates compared with the (a) U.S. EPA acute freshwater criterion maximum concentration allowances, with levels surpassing criterion marked in orange and (b) average literature EC50 values of each metal to *Daphnia magna*, with levels surpassing the EC50 marked in blue

Element (mg/L)	Mono Powder	Mono EN-B	Mono JB-C	Multi Powder	Multi EN-B	Multi JB-C	MonoFlex Powder	MonoFlex EN-B	MonoFlex JB-C	EPA Water Quality Criteria[a]	EC50 to *Daphnia Magna*[b]
Ag	27.964	112.768	0.858	92.921	96.530	2.448	24.923	89.781	1.089	0.0032	0.001
Al	3.047	1.017	0.218	78.443	15.519	0.211	100.741	4.732	0.240		2.495
As	0.006	0.002	0.000	0.001	0.002	0.000	0.006	0.000	0.000	0.34	4.767
Ba	0.003	0.017	0.006	0.043	0.007	0.005	0.001	0.005	0.002		12.750
Cd	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.0018	0.090
Co	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000		0.910
Cr	0.001	0.000	0.002	0.005	0.000	0.010	0.000	0.003	0.002	0.57	2.405
Cs	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000		5.800*
Cu	0.103	0.072	0.183	5.099	0.162	0.105	0.068	1.493	1.276		0.173
Fe	0.044	0.038	0.106	1.136	0.042	0.077	0.022	0.081	0.113		20.650
Hg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.066
Mn	0.005	0.001	0.004	0.030	0.001	0.002	0.000	0.002	0.002		9.550
Mo	0.000	0.000	0.000	0.001	0.001	0.000	0.002	0.000	0.000		1500*
Ni	0.000	0.002	0.004	0.019	0.001	0.019	0.000	0.008	0.008	0.47	0.930
Pb	0.058	0.067	0.005	1.723	0.211	0.020	0.029	1.911	0.006	0.065	1.930
Sb	0.229	0.064	0.003	0.279	0.128	0.001	0.306	0.091	0.002		4.100*
Sn	0.129	0.071	0.064	0.946	0.415	0.080	1.700	0.158	0.118		6.200*
Ti	0.005	0.005	0.001	0.306	0.004	0.002	0.002	0.007	0.002		5.700*
Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.390*
V	0.054	0.066	0.000	0.009	0.032	0.000	0.039	0.001	0.000		1.200*
W	0.004	0.002	0.003	0.002	0.007	0.001	0.010	0.001	0.001		30.000*
Zn	0.033	0.011	0.057	1.030	0.017	0.027	0.009	0.130	0.137	0.12	0.545

* Metals with only one publication in averaged literature value

Sources used in literature EC50 values: (Biesinger & Christensen, 1972; Meng et al., 2008; Oikari et al., 1992; Okamoto et al., 2015; Traudt et al., 2017; Vorobieva et al., 2020)

3.3.3 Microplastic Leaching

Microplastics were also investigated as a possible source of ecotoxicity. To the authors' best knowledge, this study represents the first attempt to examine microplastic leaching from PV modules. Duplicate 50 mL samples of each leachate were filtered and analyzed with ATR-FTIR and Raman spectroscopy. Raman microscopy, at 100x magnification, was additionally employed to determine particle sizes, with microplastics classified in the 1 to 1000 µm size (Hartmann et al., 2019).

Despite multiple attempts at characterization using ATR-FTIR, viable results were not obtained. The only identifiable peaks across all samples corresponded to nylon 6-6 or silicate glass. A comparison with readings of untested filter paper, which consisted of nylon membranes, produced identical characteristics curves as the sample papers. Therefore, the nylon 6-6 peaks were disregarded as they originated from the filter paper rather than the sample itself. The silicate glass peak was consistently present in all powder and EN-B samples, aligning with the glass and cell area collected. No additional plastic peaks were identified.

ATR-FTIR readings were corroborated by Raman characterization of the powder and EN-B filtered samples (Figure 4). The only significant peak observed across all three modules appeared at 500 cm^{-1}, which is indicative of silicate glass. In the absence of other peaks, there was no evidence of short-term leaching of microplastics from the powder or EN-B components from any module. Any extensions of this work should explore long-term procedures to determine whether the polymers in the encapsulation and back sheet degrade into microplastics over time.

However, the JB-C leachates showed microplastic contamination with multiple particles smaller than 50 µm. Significant spectral peaks were detected across various data ranges from the microscopically observed particles, with each module displaying a consistent pattern up to 2000 cm^{-1}. These smaller peaks were identified as characteristic of nylon, which were again attributed to the filter paper. Additionally, significant peaks were observed in the asymmetric hydrocarbon (C-H) region at 2800-3100 cm^{-1} (Snyder et al., 1978). The C-H region corresponds to the methyl group within polypropylene (PP), polyethylene (PE), and polyethylene terephthalate (PET), which exhibit characteristic bending vibrations in this range (Gopanna et al., 2019; Käppler et al., 2015). Previous studies have shown that microplastics can increase mortality rates and decrease growth rates in daphnid ecotoxicological assessments due to rapid absorption (Samadi et al., 2022). Consequently, the presence of methyl group plastics could contribute to the acute toxicity observed in each JB-C leachate.

While the JB-C leachates had the smallest metal concentrations overall, there was a strong indication of C-H group plastics. Hydrocarbon exposure to aquatic species was associated with mortality, developmental defects, impaired immune functions, and genetic damage (Ucan-Marin, 2015). The material in this range, in combination with the low metal concentrations, must have caused the ecotoxicity from JB-C leachates.

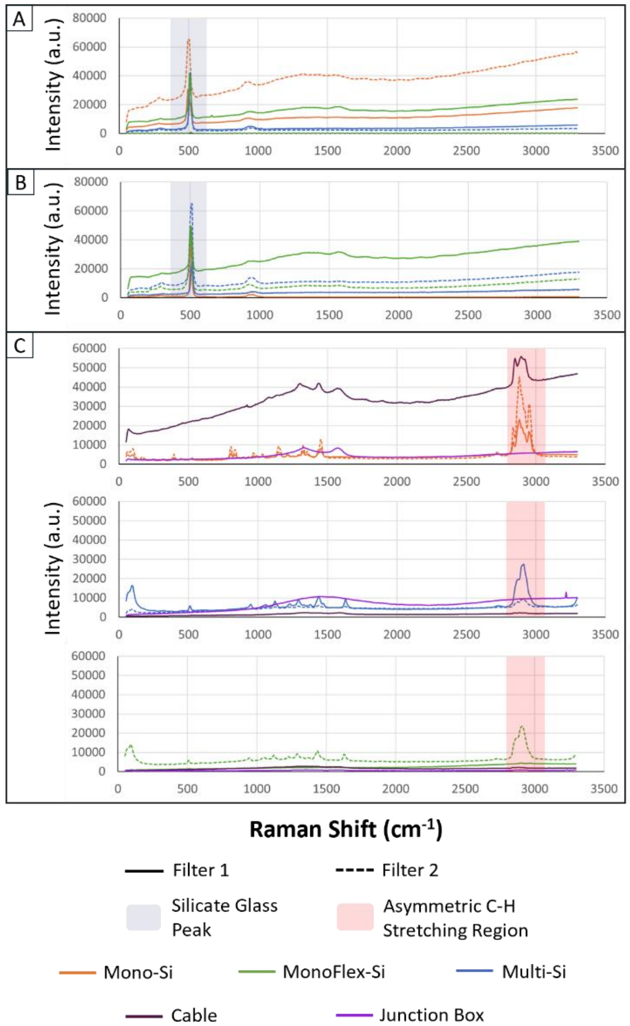

Figure 4. Raman shift curves for leachates in which a representative curve for two filtered samples is shown for the (A) powder, (B) EN-B, and (C) JB-C for each module, as well as notable peak and region markings

3.4 Final Assessment and Conclusions

In short, the acute toxicity data verifies previous c-Si toxicity assessments by confirming the presence of multiple metal elements in concentrations exceeding recommended and literature values. With no evidence of short-term plastic release from powder or EN-B leachates, the observations confirmed semiconductor metal leaching as the primary source of ecotoxicity. However, the study did identify a microplastic risk from the JB-C leachates. Microplastics can bind to heavy metals in aqueous environments, creating synergistic ecotoxicity effects (Adeleye et al., 2024). Therefore, the acute toxicity observed in JB-C leachates may be explained by metal and plastic leaching. Plastic leaching from c-Si modules should be expanded in future works to comprehensively understand the interactions between heavy metals from the cells, busbars, and solders with polymers.

An analysis of variance (ANOVA) was performed with Minitab software to compare the acute toxicity results for significance statistically. The p-value and mean of response were compared for three parameters at three levels: PV type (Mono-Si, Multi-Si, and MonoFlex-SI), component type (powder, EN-B, and JB-C), leachate concentration levels (1%, 10%, and 100%), and their corresponding interactions. The PV type and concentration parameters had high significance with p-values of 0.003 and 0.002, respectively. While the PV component itself did not have a high significance at 0.242, the interaction between the component and PV type or component and concentration did with values of 0.016 and 0.045, respectively. This indicated that the component for testing had a significant impact on response when either the type or concentration tested was accounted for. The ANOVA results, therefore, confirm that the PV type, component, and concentration all impact the toxicity results analyzed.

A means of response analysis was used to compare parameters. A Tukey 95% confidence interval difference of means analysis was performed to understand the statistical significance between levels of the same parameter (Figure 5). The results showed that the Mono-Si and Multi-Si modules were significantly different than the MonoFlex-Si module. The statistical difference verifies that the MonoFlex-Si module had the strongest impact on daphnids. The concentration levels at 100% were also significantly different from the 1% and 10% concentrations. The lack of significance between 1% and 10% indicated that dilution of the leachate reduced the impact on response. Interactions between parameters were also compared (Figure 6). The MonoFlex-Si module had the highest mean responses to the powder and EN-B leachates, but the lowest response to the JB-C as compared with the Mono-Si and Multi-Si modules. The MonoFlex-Si module also had the highest percent mean response with each concentration, again verifying the significance of the module. Of the concentrations, the 1% dilution had the highest mean response, indicating that the low concentration level was critical to evaluating c-Si toxicity.

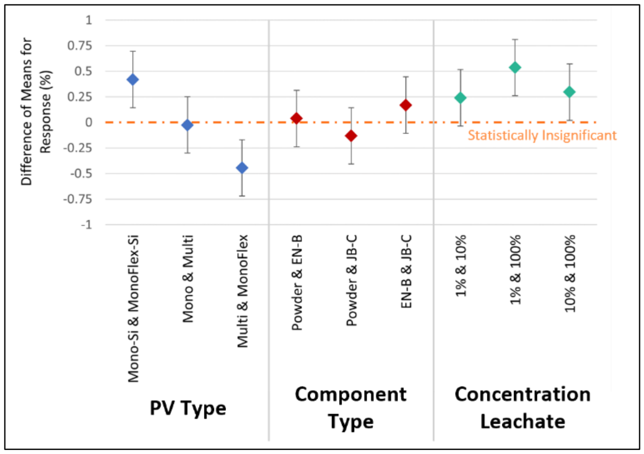

Figure 5. Tukey difference of means for response (%) evaluating a 95% confidence interval for statistical significance for ANOVA parameters

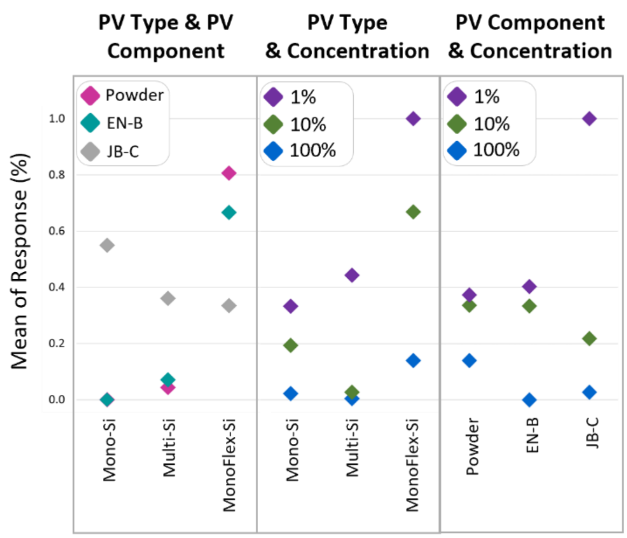

Figure 6. Interaction comparison analysis displaying the percent mean of response when comparing two parameters of investigation

In conclusion, the acute toxicity of c-Si modules can vary based on the module type, the specific waste components exposed, and the concentration of leached substances, including both metal and microplastic leaching. Even when evaluating the same PV technology, the environmental impact demonstrated variability and warrants careful consideration as PV waste accumulates. To mitigate these impacts, extensive recycling efforts should be prioritized, and illegal open dumping must be eliminated to prevent contamination of surface waters and subsequent adverse effects on aquatic wildlife.

Chapter 4: Column Study Design and Construction for Partially Recycled c-Si Waste

4.1 Simulated landfills in Literature

To evaluate the impact of landfill leachate exposure, the acute toxicity study of components was expanded by testing landfill effluents with *Daphnia magna*. Previous modelling approaches included fate and transport software and batch leaching procedures to evaluate the landfill leaching potential of metals (Nain & Kumar, 2020b; Sinha et al., 2014). This study aims to build laboratory scale landfill columns to experimentally investigate the impact of c-Si landfill leachates. The following literature review discusses the experimental set up of similar studies.

Few researchers have designed laboratory scale landfill models to investigate real leachate production from PV modules. Ramos-Ruiz et al. tested a cadmium telluride (CdTe) module with upflow columns (Ramos-Ruiz et al., 2017). Columns of 280 mL in volume had a continuous pumped inflow of a synthetic leachate solution from the bottom, with valves for effluent collection and gas release at the top. Two columns were packed with layers of CdTe waste (snipped CdTe film and crushed glass) and granular sludge. The pH, soluble cadmium and tellurium, volatile fatty acids (VFA), and chemical oxygen demand (COD) were tracked for 30 days. In comparison, Kilgo et al. tested a c-Si module by mixing it with simulated municipal solid waste (Kayla Kilgo et al., 2022). The simulated waste contained paper, plastic, metal, glass, and food and was mixed with sandy loam soil. The composite mixture was placed in a container and covered with pea gravel to maintain compaction, then saturated with simulated landfill leachate. The redox potential and pH were tracked for 100 days. Metals of both liquid aliquots and biofilms were measured. While the two research groups had different designs for the landfill model, both included additive waste components. The use of sludge or simulated waste provided perspective of a real landfill, as the system would include many types of waste.

While very few papers have evaluated PV waste with simulated landfills, multiple publications used the methodology to investigate other types of electronic waste (Intrakamhaeng et al., 2020; Kiddee et al., 2013; Li et al., 2009; Spalvins et al., 2008). Two groups testing electronic waste used lysimeter columns. Intrakamhaeng et al.'s lysimeter design used 6 ft stainless steel pipes of 6 inches in diameter (Intrakamhaeng et al., 2020). The researchers packed the lysimeter with television plastic cases and a synthetic municipal solid waste (MSW) mixture of food waste, plastics, paper, yard trimmings, metals, and glasses. Each lysimeter had ports for adding water, but the watering schedule was not specified. The primary goal of the study was to analyze antimony mobility from the electronic plastic waste, but also tested the dissolved oxygen, pH, alkalinity, VFAs, specific conductivity, and COD. When the electronic waste was included in the lysimeter, antimony concentrations were much higher than in controls. Spalvins et al.'s model consisted of two 16.5 ft high-definition polyethylene (HDPE) pipes. A 3 inch in diameter pipe was used within the 24 inch in diameter column for aliquot collection (Spalvins et al., 2008). The column was packed with various electronic wastes (central processing unit, keyboard, mouse, cathode ray tube, cell phones, and smoke detectors) in combination with a similar MSW mixture of paper, food, plastic, glass, metal, and yard waste. Irrigation tubing was used to add between 680 L and 970 L of tap water on 25 to 30 occasions. The study primarily analyzed Pb leaching, but also looked at alkalinity, total dissolved solids, nonpurgeable organic carbon, biochemical oxygen demand (BOD), COD, and VFAs. When compared with the TCLP test, the Pb concentrations from the lysimeter leachates were much lower and suggested that Pb was not of regulatory concern. Once again, studies with similar goals of analyzing electronic waste with simulated municipal waste, had different designs and testing parameters. Despite varying methodologies, both could estimate the goals of study.

Other studies had much smaller systems constructed of HDPE to test electronic waste (Kiddee et al., 2013; Li et al., 2009). Li et al. tested personal computer components, including the motherboard, expansion car, disc drive, and more (Li et al., 2009). The columns were 2 m in height and 0.5 m in diameter, with a sharply sloped bottom for drainage collection from the middle of the system as shown in part A of Figure 6. While the previously discussed lysimeters were completely sealed off, this design was topped with a gravel layer, geotextile fabric, then a soil layer with a water distributor as an influent source. Within the column, the electronic waste was placed between two layers of MSW. Precipitation events were simulated by adding approximately 30 mm of tap water to the top of the column weekly, which was representative of a wet U.S. region. The effluent was collected weekly, with volume recorded. Aliquots of the effluent were collected monthly and analyzed over a two-year period for pH, total organic carbon, oxidation reduction potential, and 18 elements. At the end of the experiment, Al, barium (Ba), Cu, Fe, and Zn were detected, with Fe leaching at the highest concentration of 4.5 mg/L. To compare, Kiddee et al. also used a column of 2 m in height but was of wider diameter at 1.8 m (Kiddee et al., 2013). The constructed column was left outside in South Australia on a slightly sloped concrete base. The columns were packed with a 100 mm layer of gravel, then a geotextile fabric, followed by a 1.35 m mix of municipal solid waste and electronic waste, and topped with a 50 mm layer of gravel as shown in part B of Figure 7. The column was left open to natural rain events. The leachate was collected monthly for analysis of pH, oxidation reduction potential, electrical conductivity, total dissolved solids, total organic carbons, 14 metals, and polybrominated diphenyl ethers. Columns with electronic waste had higher average concentrations of multiple metals but did not reach levels of regulatory concern and showed much lower concentrations than typical of TCLP extractions. The two designs provided valuable expectations for the set up and results in testing electronic waste at a smaller scale.

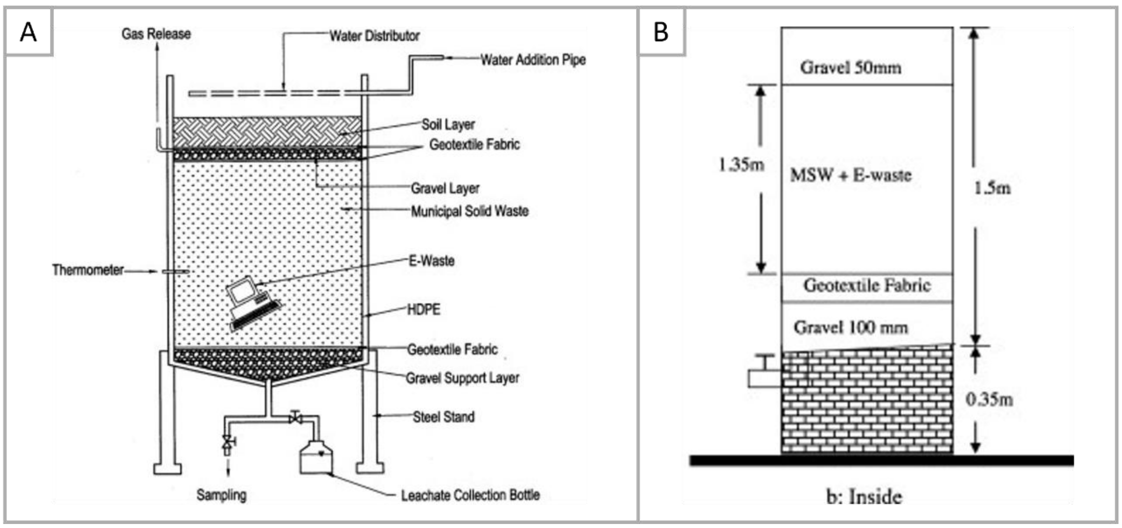

Figure 7. Schematics of landfill simulation columns from (A) Li et al., (2009) and (B) Kiddee et al., (2013)

Previous efforts to characterize electronic waste with simulated landfill columns were highly variable. Each research group had different parameters for column volume, layering, watering schedules, and experimental length. Due to the lack of commonality between studies, the literature review was expanded to publications focused on the leaching behavior of landfills in the absence of additional waste (Choi et al., 2016; Sarmah et al., 2024). Choi et al. designed a simple plastic cylinder of 10 cm in height and 5 cm in diameter for testing an Ottawa sand with fiber reinforcement (Choi et al., 2016). A 7% water distilled water content was added and the sand mixture was compacted in 10 layers of 1 cm each. The column had a sloped bottom filled with gravel, which was covered with a filter, the sample mixture, then another filter. The effluent was pumped back in as influent, as the parameters of investigation included calcium carbonate content, permeability, and strength of the soil rather than investigating waste leachate. Sarmah et al. studied the environmental safety of inert landfills with two columns of height 153 cm and diameter 30 cm

(Sarmah et al., 2024). The tube had a 10 cm layer of soil on the bottom, then two 40 cm layers of fibrous content received from an inert landfill separated and topped with additional 10 cm layers of soil. There were three leachate collection points of 40 cm and 80 cm from the top and at the bottom. Distilled water was added to the top of the column to reflect the annual rainfall in Japan of 1530 mm/year. The publications from Choi et al. and Sarmah et al. served as inspiration for the following study.

In summation, column studies varied widely. Designs spanned from less than 5 inches in height to over 16 feet with diameters from 2 to 24 inches. Layering patterns also greatly differed, as some studies used gravel and soil barriers, while others had one composite mixture. Watering schedules also varied as some researchers modelled the precipitation patterns of a region, some simply added enough for analysis, and others had continuous pumping. Due to the diverse set ups discussed, the following study had few concrete guidelines from literature. The design therefore aimed to simplify the column and focus on the impact of waste.

4.2 Column Design and Waste Scenario Methodology

The designed column needed to reflect the characteristics of an MSW landfill. MSW locations are required to use a compacted clay liner (CCL) with a minimum thickness of 600 mm (23.6 in) and hydraulic conductivity of less than 1×10^{-7} cm/sec (Vishnupriya & Rajagopalan, 2022). Click or tap here to enter text.The average MSW landfill compacts 1300 to 1600 lbs. of garbage into cells of one cubic yard (Michigan Department of Environment, 2022), whereas the following study was meant to evaluate the impact of 100 g of c-Si waste. The scale was therefore reduced to a column of diameter 2.5 inches and height of 18 inches, as seen in Figure 8. The column was packed with an approximate 3-inch layer of river pebbles, a 3-inch layer of soil, then two layers of c-Si waste each topped with 1-inch layers of soil. A total of eight columns were constructed to allow for two control columns and three testing scenarios for two different c-Si modules.

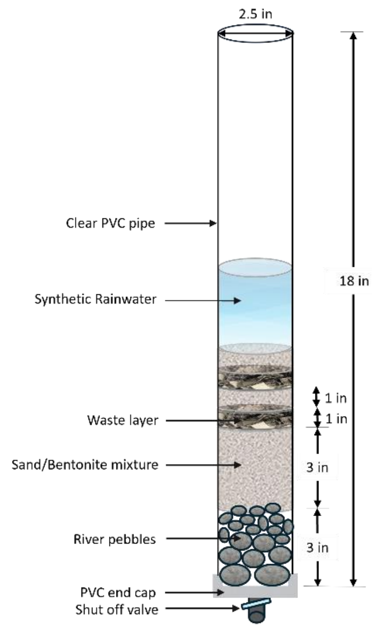

Figure 8. Schematic design for column showing dimensions of the overall column, the soil and clay mixture, and the included waste layer

The c-Si waste of the Renogy monocrystalline (Mono) and ACOPOWER multicrystalline (Multi) modules outlined in Section 3.2.1 were used for testing. The aluminum frame of each module was removed with a circular saw, then the remaining module was water jet cut into strips of 1 inch width. Three scenarios were defined to compare the potential leachability of partially recycled waste (Figure 9). The first scenario reflected no recycling, in which the entire module was dumped in a landfill. Strips from each module were shear cut into squares of approximately 0.5x0.5 in^2 for a total mass of 100 g. The aluminum frame was also cut into pieces of 0.5x0.5 in^2 with a bandsaw for a total mass of 20 g, as frames were 20% of overall c-Si module mass on average (Frischknecht et al., 2020). The resulting 120 g was evenly distributed as the waste layer in the column. The second scenario reflected a standard mechanical recycling procedure, in which the glass was crushed, and the aluminum frame was removed. For this scenario, 100 g of shear cut module squares were crushed with a mortar-pestle to remove the glass layer. All glass was then sieved out with a standard No. 8 sieve and the resulting waste was used in the column. The third scenario was meant to reflect the removal of the semiconductor layer with all polymer material sent to landfill. Again, 100 g of shear cut squares were crushed, but grinding continued until all semiconductor material was removed from the encapsulation and back sheet polymers. The resulting waste was sieved with a standard No. 4 sieve to separate the polymers and plastics from any remaining semiconductor or glass particles.

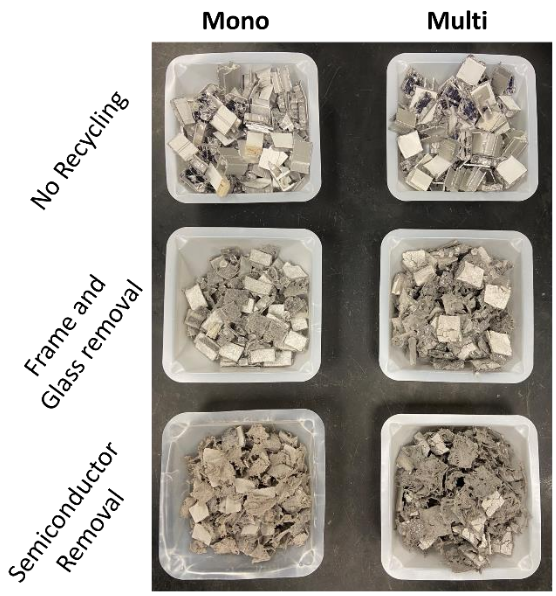

Figure 9. Outlined scenarios for c-Si module recycling for column waste layer

Previous studies used synthetic MSW mixtures in addition to the waste of interest to mimic exposure to many types of waste. This study simplified the setup by focusing on the c-Si waste scenarios without additives. The design therefore allowed for evaluation of contaminants solely sourced from the waste of interest. Analysis could then provide direct comparisons of potential exposure from the selected waste variations and type of module to the environment.

To mimic the characteristics of an MSW landfill, the soil was characterized for gradation, compaction, and hydraulic conductivity. Natural liners use a clayey soil type, which could be developed with a mixture of bentonite and sandy soil (Cossu, 2018). The mixture should be well graded to allow for sufficient compaction and to prevent erosion (Technical Reference Document for Liquid Manure Storage Structures Compacted Clay Liners, 2007). Ottawa density test sand was mixed with pure bentonite clay at 10%, 20%, and 30% clay concentrations and tested to determine the optimum content as per MSW regulations. Each concentration was first assessed by ASTM D1140-17 (American Society for Testing and Materials, 2017) for determination of material finer than 75 µm. Non-passing particles were dried at 102ºC for 24 hours, then sieved with standard No. 20, 40, 100, and 200 sieves in a Gilson Silent Sifter for 10 minutes. The gradation curve was then developed as seen in Figure 10 and the coefficients of uniformity and curvature were calculated. Each clay concentration was then subjected to a compaction test under ASTM D698-12 (American Society for Testing and Materials, 2021) and graphed as shown in Figure 11.

Lastly, using the optimum water content observed in compaction, each concentration was tested for hydraulic conductivity with ASTM standards D2434-22 and D5084-16a (American Society for Testing and Materials, 2016, 2022). The complete data set was used to determine the optimum clay content to mimic an MSW landfill.

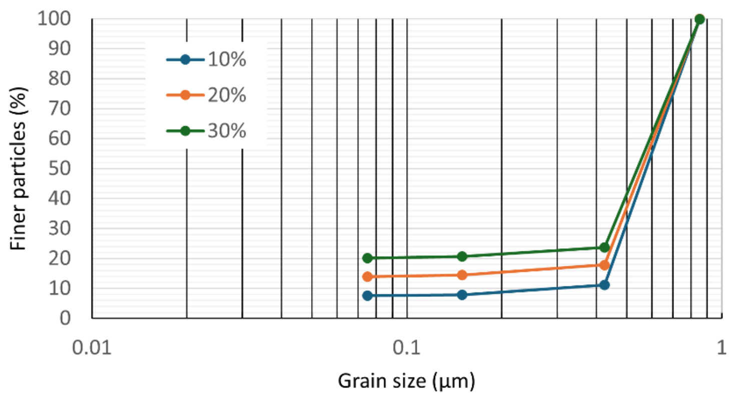

Figure 10. Gradation curves for 10%, 20%, and 30% clay concentrations showing the percentage of finer particles in the mixture based on the grain size

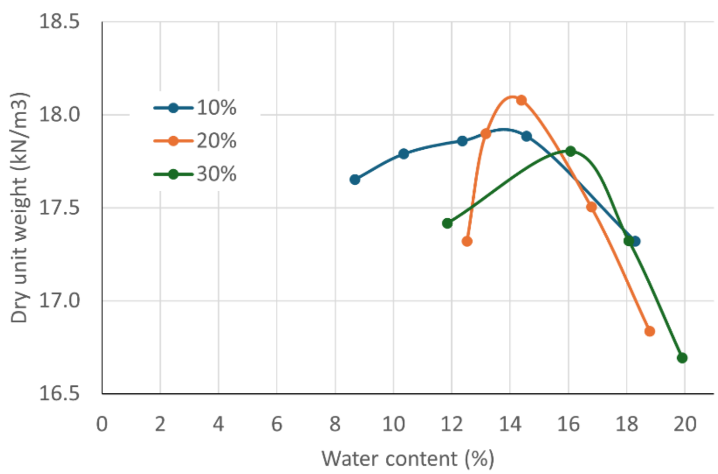

Figure 11. Compaction curves for 10%, 20%, and 30% clay concentrations

The final clay to sand composition was based on optimum gradation, compaction, and hydraulic conductivity. To analyze the gradation curve, the coefficients of uniformity (C_u) and curvature (C_c) were calculated based on Equation 1 and 2 respectively, in which d was the diameter of grain size for a specified percentage of passing particles.

$$C_u = {d_{60}}/{d_{10}} \tag{1}$$

$$C_c = {(d_{30})^2}/{d_{10}d_{60}} \tag{2}$$

A well graded soil must have a C_u greater than 6 for sands and a C_c between 1-3 (Kalore & Sivakumar Babu, 2023). Based on the calculated uniformity coefficients shown in Table 6, the 20% and 30% clay concentrations were optimal for gradation but had curvature coefficients higher than 3. The 10% concentration had a coefficient of curvature within range but a low uniformity coefficient. The optimum content based on gradation therefore fell between 10% and 20%.

Table 6. Parameter results for gradation, compaction, and hydraulic conductivity testing

Parameter	10% Clay	20% Clay	30% Clay
Coefficient of Uniformity	2.03	8.00	7.87
Coefficient of Curvature	1.37	4.70	4.58
Optimum Water Content (%)	14	14	16
Hydraulic Conductivity (cm/s)	7.0E-07	2.5E-07	1.2E-07

For compaction testing, the curves shown in Figure 10 indicated the optimum water content for the mixture based on the dry unit weight. The optimum water content allowed for the maximum weight of the soil and therefore the minimum size of pores between grains. By minimizing the pore size, the compacted mixture increased shear strength through friction between particles, preventing erosion (Attom, 1997). In addition to optimum water content, the curve indicated the type of soil. Poorly graded soil has a flatter curve, such as seen in the 10% concentration, as uniform particles have little ability to fill the pores between grains. Higher peaks indicate well graded soils, but sharp curves like that of the 20% concentration may be more sensitive to environmental changes. Based on the graphed concentrations, the optimal percentage again fell between 10% and 20% to mediate the gradation and sensitivity to changes. The maximized dry unit weight then allowed for analysis of hydraulic conductivity. The hydraulic conductivity, as seen in Table 6, had little variation between clay concentrations. While MSW landfills were required to have a liner conductivity of less than 1×10^{-7}, the hydraulic conductivity of each concentration was close to the regulation and was justified for a lab scale model. Based on the three parameters, a 15% concentration of clay was selected to optimize gradation coefficients and mediate the compaction curve.

4.3 Experimental Setup

After schematic conception, the columns were built out of PVC pipes and fittings (Figure 12). All pieces were sealed with PVC primer and glue to prevent leakage during experimentation.

The 15% bentonite to 85% sand mixture was prepared and saturated at 14% by mass with tap water based on the optimized parameters discussed in Section 4.2. The river pebbles were placed in the bottom, then covered with the sand mixture. The sand was compacted with a wooden dowel of 1-inch in diameter and the waste was placed in even layers.

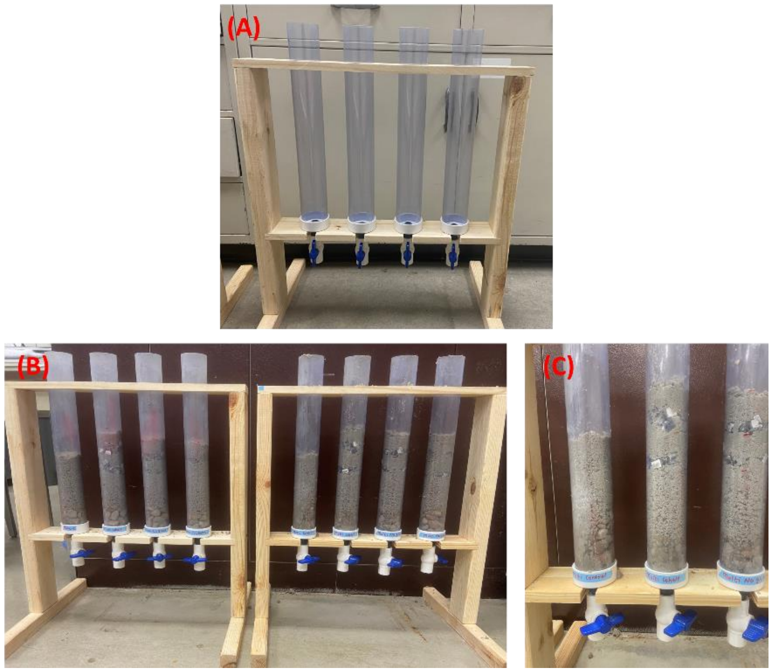

Figure 12. Constructed columns (A) before fill, (B) after complete fill, and (C) close-up of packed levels

Each column was watered weekly to simulate precipitation events in Michigan with volume based on accelerated exposure to monthly rainfall. A 3.2 inch per month precipitation rate was used, so 400 mL were added each week. The rainwater was simulated with 10.5 g/L citric acid ($C_6H_8O_7$) and 1.7 g/L disodium hydrogen phosphate dissolved in deionized water for a pH of 4.0±0.1. The column was allowed to percolate for four days, then leachate was collected in a 1 L beaker from the bottom valve. Each week, the leachate was digested by EPA Method 3005A for ICP-MS element analysis. The pH, alkalinity, hardness, and acidity were also tracked. The ongoing project will run for a one-month study.

Chapter 5: Conclusion

As PV installations become ever more important as a green energy source, module's EOL must also be considered. Due to the use of various critical and hazardous metals used in c-Si modules, environmental toxicity has been the focus of multiple publications. However, previous researchers only analyzed the semiconductor layer as a source of ecotoxicity. This work investigated three categorized components from three c-Si modules, the Renogy monocrystalline (Mono-Si), ACOPOWER Multicrystalline (Multi-Si), and Renogy semi-flexible monocrystalline (MonoFlex-Si). The components of consideration, the powdered glass and cell areas (powder), encapsulation and back sheet polymers (EN-B), and junction box and cables (JB-C), were each subjected to aquatic toxicity bioassays with *Daphnia magna*. The half maximal effective concentration (EC50) was determined based on daphnid immobilization response to component leachates.

Acute toxicity results varied between tested modules and components. The powder and EN-B leachates for the Mono-Si module were the least toxic with no response, while the Multi-Si module had little response, and the MonoFlex-Si sharp responses. The Mono-Si module did not cause immobility at any tested concentration for the powder or EN-B under the standard U.S. EPA bioassay protocol. However, when the powder was tested without a pH adjustment, there was an observed response with an EC50 at a 61% leachate concentration. The Multi-Si module had projected EC50's of 181% and 127% to the powder and EN-B respectively. Again, without a pH adjustment, the powder response escalated to a significant EC50 at 0.6% leachate. The intensified responses to unadjusted powder leachates suggested a relationship between pH and toxicity of contaminants. Lastly, the MonoFlex-Si had highly significant results with EC50s of 0.2% and 5% to the powder and EN-B. The JB-C leachate responses opposed the pattern observed with the powder and EN-B leachates. The Mono-Si module had the sharpest response at 9% and the MonoFlex-Si the least 52%, while the Multi-Si again fell in the middle at 27%.

Both metal elements and microplastics were investigated as potential sources of ecotoxicity. The metals of highest significance were Al, Ag, Cu, and Zn due to concentrations leached at levels above the acute toxicity level reflected by literature. Pb was also of notable concern, as some leachate concentrations surpassed the EPA acute aquatic water criteria level. Short-term microplastic leaching was of little concern for the powder and EN-B mixtures, as no evidence of plastic was found in ATR-FTIR or Raman spectroscopy data. The JB-C leachates did however show evidence of hydrocarbons, which are characteristics of methyl polymers such as polypropylene and polyethylene. The metal leaching in the powder and EN-B leachates was the primary source of ecotoxicity, but the microplastics in JB-C leachates may have contributed. Future work should include long-term leaching procedures to expand on microplastic analysis.

As an expansion of c-Si component analysis, a landfill column study was designed to investigate the impact of recycling procedures on remaining waste. The column was built of PVC piping and accessories for a simplistic laboratory scale model. The packing soil included density test sand mixed with 15% pure bentonite clay based on the parameters of gradation, compaction, and hydraulic conductivity analysis. The c-Si waste of the Mono-Si and Multi-Si modules were added in three scenarios of disposal: no recycling, glass and Al frame removal, and semiconductor removal. The experimental watering schedule was based on the precipitation rates of wet U.S. regions, in which each week a monthly precipitation amount was added to simulate an accelerated impact. The ongoing experiment will test the metal leaching, pH, alkalinity, hardness, acidity, and acute toxicity of leachates.

The experimental research discussed showed the importance of a circular economy in the green energy sector. Waste management must be considered as solar technology usage rises, with recycling prioritized. This research showed the potential risk of both metals and microplastics from c-Si modules to the aquatic environment in a worst-case scenario of open dumping. Without designated regulations governing module waste or infrastructure to collect it, the potential for exposure rises.

BIBLIOGRAPHY

Adekanmbi, A. O., Ninduwezuor-Ehiobu, N., Izuka, U., Abatan, A., Ani, E. C., & Obaigbena, A. (2024). Assessing the environmental health and safety risks of solar energy production. *World Journal of Biology Pharmacy and Health Sciences*, *2024*(02), 225–231. https://doi.org/10.30574/wjbphs.2024.17.2.0080

Adeleye, A. T., Bahar, M. M., Megharaj, M., Fang, C., & Rahman, M. M. (2024). The Unseen Threat of the Synergistic Effects of Microplastics and Heavy Metals in Aquatic Environments: A Critical Review. *Current Pollution Reports*, 1–20. https://doi.org/10.1007/S40726-024-00298-7/TABLES/3

Aguado-Monsonet, M. A. (1998). The environmental impact of photovoltaic technology. In *Institute for Prospective Technological Studies Seville*. https://www.ctc-n.org/sites/www.ctc-n.org/files/resources/environmental_impact_of_pv_tech.pdf

American Society for Testing and Materials. (2016). *ASTM D5084-16a Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter*.

American Society for Testing and Materials. (2017). *ASTM D1140-17 Standard Test Methods for Determining the Amount of Material Finer than 75 μm (No. 200) Sieve in Soils by Washing*.

American Society for Testing and Materials. (2021). *ASTM D698-12 Standard Test Methods for Laboratory Compaction Characteristics of Soil Using Standard Effort*.

American Society for Testing and Materials. (2022). *ASTM D2434-22 Standard Test Methods for Measurement of Hydraulic Conductivity of Coarse-Grained Soils*.

Attom, M. F. (1997). The effect of compactive energy level on some soil properties. *Applied Clay Science*, *12*(1–2), 61–72. https://doi.org/10.1016/S0169-1317(96)00037-3

Bang, Y. Y., Hong, N. J., Sung Lee, D., & Lim, S. R. (2018). Comparative assessment of solar photovoltaic panels based on metal-derived hazardous waste, resource depletion, and toxicity potentials. *International Journal of Green Energy*, *15*(10), 550–557. https://doi.org/10.1080/15435075.2018.1505618

Bianchini, A., Grosell, M., Gregory, S. M., & Wood, C. M. (2002). Acute silver toxicity in aquatic animals is a function of sodium uptake rate. *Environmental Science and Technology*, *36*(8), 1763–1766. https://doi.org/10.1021/ES011028T/ASSET/IMAGES/LARGE/ES011028TF00002.JPEG

Biesinger, K. E., & Christensen, G. M. (1972). Effects of Various Metals on Survival, Growth, Reproduction, and Metabolism of Daphnia magna. *U.S. Environmental Protection Agency National Water Quality Laboratory*, *10*.

Biesinger, K. E., Williams, L. R., & Van der Schalie, W. H. (1987). *Procedures for Conducting Daphnia magna Toxicity Bioassays*. U.S. Environmental Protection Agency. https://nepis.epa.gov/Exe/ZyNET.exe/2000AY11.txt?ZyActionD=ZyDocument&Client=EP

A&Index=1986%20Thru%201990&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C86THRU90%5CTXT%5C00000001%5C2000AY11.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=2

Brown, F. C., Bi, Y., Chopra, S. S., Hristovski, K. D., Westerhoff, P., & Theis, T. L. (2018). End-of-Life Heavy Metal Releases from Photovoltaic Panels and Quantum Dot Films: Hazardous Waste Concerns or Not? *ACS Sustainable Chemistry and Engineering*, *6*(7), 9369–9374. https://doi.org/10.1021/ACSSUSCHEMENG.8B01705

California Waste Extraction Test, Pub. L. No. 78- 1800.82 (1985).

Choi, S. G., Wang, K., & Chu, J. (2016). Properties of biocemented, fiber reinforced sand. *Construction and Building Materials*, *120*, 623–629. https://doi.org/10.1016/J.CONBUILDMAT.2016.05.124

Collins, M. K., & Anctil, A. (2017). Implications for current regulatory waste toxicity characterisation methods from analysing metal and metalloid leaching from photovoltaic modules. *International Journal of Sustainable Energy*, *36*(6), 531–544. https://doi.org/10.1080/14786451.2015.1053392

Cossu, R. (2018). Physical Landfill Barriers: Principles and Engineering. *Solid Waste Landfilling*, 271–287. https://doi.org/10.1016/B978-0-12-407721-8.00015-2

Curtis, T. L., Buchanan, H., Heath, G., Smith, L., & Shaw, S. (2021). *Solar Photovoltaic Module Recycling: A Survey of U.S. Policies and Initiatives*. https://www.nrel.gov/docs/fy21osti/74124.pdf

Dagan, R., Dubey, B., Bitton, G., & Townsend, T. (2007). Aquatic toxicity of leachates generated from electronic devices. *Archives of Environmental Contamination and Toxicology*, *53*(2), 168–173. https://doi.org/10.1007/S00244-006-0205-1/TABLES/5

Davis, M., Leyva Martinez, S., Gaston, Z., Chopra, S., Connelly, C., Fung, K., Issokson, M., Pierce, E., Colombo, A., Rumery, S., Silver, C., Thompson, T., & Baca, J. (2024). *US Solar Market Insight Executive Summary 2023 Year in Review*. www.woodmac.com/research/products/power-and-renewables/us-solar-market-insight/.

Deline, C., Jordan, D., Sekulic, B., Parker, J., Mcdanold, B., & Anderberg, A. (2021). *PV Lifetime Project - 2021 NREL Annual Report*. https://www.nrel.gov/docs/fy22osti/81172.pdf

Dominish, E., Teske, S., & Florin, N. (2019). *Responsible Minerals Sourcing for Renewable Energy*. https://earthworks.org/wp-content/uploads/2019/04/Responsible-minerals-sourcing-for-renewable-energy-MCEC_UTS_Earthworks-Report.pdf

Dubey, S., Jadhav, N. Y., & Zakirova, B. (2013). Socio-Economic and Environmental Impacts of Silicon Based Photovoltaic (PV) Technologies. *Energy Procedia*, *33*, 322–334. https://doi.org/10.1016/J.EGYPRO.2013.05.073

Eberspacher, C., & Fthenakis, V. M. (1997). Disposal and recycling of end-of-life PV modules. *Conference Record of the IEEE Photovoltaic Specialists Conference*, 1067–1072. https://doi.org/10.1109/PVSC.1997.654272

El-Deeb Ghazy, M. M., Habashy, M. M., & Mohammady, E. Y. (2011). Effects of pH on Survival, Growth and Reproduction Rates of The Crustacean, Daphnia Magna. *Australian Journal of Basic and Applied Sciences*, *5*(11), 1–10.

Experiment 2-3 Qualitative Analysis of Metal Ions in Solution. (n.d.).

Fargasova, A. (1994). Toxicity of Metals on Daphnia magna and Tubifex tubifex. *Ecotoxicology and Environmental Safety*, *27*(2), 210–213. https://doi.org/10.1006/EESA.1994.1017

Frischknecht, R., Stolz, P., Krebs, L., de Wild-Scholten, M., & Sinha, P. (2020). *Life Cycle Inventories and Life Cycle Assessments of Photovoltaic Systems*. www.iea-pvps.org

Gopanna, A., Mandapati, R. N., Thomas, S. P., Rajan, K., & Chavali, M. (2019). Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and wide-angle X-ray scattering (WAXS) of polypropylene (PP)/cyclic olefin copolymer (COC) blends for qualitative and quantitative analysis. *Polymer Bulletin*, *76*(8), 4259–4274. https://doi.org/10.1007/S00289-018-2599-0/FIGURES/10

Hartmann, N. B., Hüffer, T., Thompson, R. C., Hassellöv, M., Verschoor, A., Daugaard, A. E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herrling, M. P., Hess, M. C., Ivleva, N. P., Lusher, A. L., & Wagner, M. (2019). Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris. *Environmental Science and Technology*, *53*(3), 1039–1047. https://doi.org/10.1021/ACS.EST.8B05297/ASSET/IMAGES/MEDIUM/ES-2018-05297K_0006.GIF

Intrakamhaeng, V., Clavier, K. A., Liu, Y., & Townsend, T. G. (2020). Antimony mobility from E-waste plastic in simulated municipal solid waste landfills. *Chemosphere*, *241*. https://doi.org/10.1016/j.chemosphere.2019.125042

Jana, S., & Choudhuri, M. A. (1984). Synergistic effects of heavy metal pollutants on senescence in submerged aquatic plants. *Water, Air, and Soil Pollution*, *21*(1–4), 351–357. https://doi.org/10.1007/BF00163635/METRICS

Kalore, S. A., & Sivakumar Babu, G. L. (2023). Significance of Cu and Cc in Evaluating Internal Stability with Application to Design of Subbase Gradation in Pavements. *Transportation Geotechnics*, *40*, 100972. https://doi.org/10.1016/J.TRGEO.2023.100972

Käppler, A., Windrich, F., Löder, M. G. J., Malanin, M., Fischer, D., Labrenz, M., Eichhorn, K. J., & Voit, B. (2015). Identification of microplastics by FTIR and Raman microscopy: a novel silicon filter substrate opens the important spectral range below 1300 cm−1 for FTIR transmission measurements. *Analytical and Bioanalytical Chemistry*, *407*(22), 6791–6801. https://doi.org/10.1007/S00216-015-8850-8/FIGURES/11

Kayla Kilgo, M., Anctil, A., Kennedy, M. S., & Powell, B. A. (2022). Metal leaching from Lithium-ion and Nickel-metal hydride batteries and photovoltaic modules in simulated landfill leachates and municipal solid waste materials. *Chemical Engineering Journal*, *431*, 133825. https://doi.org/10.1016/J.CEJ.2021.133825

Kiddee, P., Naidu, R., & Wong, M. H. (2013). Metals and polybrominated diphenyl ethers leaching from electronic waste in simulated landfills. *Journal of Hazardous Materials*, *252–253*, 243–249. https://doi.org/10.1016/j.jhazmat.2013.03.015

Kiger, B. (2016, April 19). *Life Cycle Assessment and Photovoltaic (PV) Recycling: Designing a More Sustainable Energy System*. State, Local, & Tribal Governments, National Renewable Energy Laboratory. https://www.nrel.gov/state-local-tribal/blog/posts/life-cycle-assessment-and-photovoltaic-pv-recycling-designing-a-more-sustainable-energy-system.html

Krishnamurthy, R. (2017). *Standardized Sample Extraction Procedure for TCLP Testing of PV Modules*. Arizona State University.

Kwak, J. Il, Kim, L., Lee, T. Y., Panthi, G., Jeong, S. W., Han, S., Chae, H., & An, Y. J. (2021). Comparative toxicity of potential leachates from perovskite and silicon solar cells in aquatic ecosystems. *Aquatic Toxicology*, *237*, 105900. https://doi.org/10.1016/J.AQUATOX.2021.105900

Leslie, J. (2018). *Dependence of Toxicity Test Results on Sample Removal Methods of PV Modules*. Arizona State University.

Li, Y., Richardson, J. B., Mark Bricka, R., Niu, X., Yang, H., Li, L., & Jimenez, A. (2009). Leaching of heavy metals from E-waste in simulated landfill columns. *Waste Management*, *29*(7), 2147–2150. https://doi.org/10.1016/j.wasman.2009.02.005

Marion, S. P., & Thomas, A. W. (1946). *Effect of Diverse Anions on the pH of Maximum Precipitation of Aluminum Hydroxide*.

Martinka, J. (2022). *Description and the Parameters of Electrical Cables*. 1–21. https://doi.org/10.1007/978-3-031-17050-8_1

Meng, Q., Li, X., Feng, Q., & Cao, Z. (2008). The acute and chronic toxicity of five heavy metals on the Daphnia magna. *2nd International Conference on Bioinformatics and Biomedical Engineering, ICBBE 2008*, 4555–4558. https://doi.org/10.1109/ICBBE.2008.298

Michigan Department of Environment, G. L. and E. (EGLE). (2022). *How Landfills Work*. https://www.michigan.gov/egle/-/media/Project/Websites/egle/Documents/Programs/MMD/Landfills/How-Landfills-Work.pdf

Mirletz, H., Hieslmair, H., Ovaitt, S., Curtis, T. L., & Barnes, T. M. (2023). Unfounded concerns about photovoltaic module toxicity and waste are slowing decarbonization. *Nature Physics 2023 19:10*, *19*(10), 1376–1378. https://doi.org/10.1038/s41567-023-02230-0

Molleman, B., & Hiemstra, T. (2017). *The pH, time, and size dependency of silver nanoparticle dissolution: the road to equilibrium*.

Motta, C. M., Cerciello, R., De Bonis, S., Mazzella, V., Cirino, P., Panzuto, R., Ciaravolo, M., Simoniello, P., Toscanesi, M., Trifuoggi, M., & Avallone, B. (2016). Potential toxicity of improperly discarded exhausted photovoltaic cells. *Environmental Pollution*, *216*, 786–792. https://doi.org/10.1016/j.envpol.2016.06.048

Nain, P., & Kumar, A. (2020a). Identifying issues in assessing environmental implications of solar PVs-related waste. *Lecture Notes in Civil Engineering*, *57*, 71–90. https://doi.org/10.1007/978-981-15-0990-2_7/TABLES/3

Nain, P., & Kumar, A. (2020b). Metal dissolution from end-of-life solar photovoltaics in real landfill leachate versus synthetic solutions: One-year study. *Waste Management*, *114*, 351–361. https://doi.org/10.1016/J.WASMAN.2020.07.004

Nain, P., & Kumar, A. (2020c). Understanding the possibility of material release from end-of-life solar modules: A study based on literature review and survey analysis. *Renewable Energy*, *160*, 903–918. https://doi.org/10.1016/J.RENENE.2020.07.034

Nover, J., Zapf-Gottwick, R., Feifel, C., Koch, M., Metzger, J. W., & Werner, J. H. (2017). Long-term leaching of photovoltaic modules. *Japanese Journal of Applied Physics*, *56*(8), 08MD02. https://doi.org/10.7567/JJAP.56.08MD02/XML

Nover, J., Zapf-Gottwick, R., Feifel, C., Koch, M., & Werner, J. H. (2021). Leaching via Weak Spots in Photovoltaic Modules. *Energies 2021, Vol. 14, Page 692*, *14*(3), 692. https://doi.org/10.3390/EN14030692

Oikari, A., Kukkonen, J., & Virtanen, V. (1992). Acute toxicity of chemicals to Daphnia magna in humic waters. *Science of The Total Environment*, *117–118*(C), 367–377. https://doi.org/10.1016/0048-9697(92)90103-Y

Okamoto, A., Yamamuro, M., & Tatarazako, N. (2015). Acute toxicity of 50 metals to Daphnia magna. *Journal of Applied Toxicology*, *35*(7), 824–830. https://doi.org/10.1002/JAT.3078

Panthi, G., Bajagain, R., An, Y. J., & Jeong, S. W. (2021). Leaching potential of chemical species from real perovskite and silicon solar cells. *Process Safety and Environmental Protection*, *149*, 115–122. https://doi.org/10.1016/J.PSEP.2020.10.035

Part 261 - Identification and Listing of Hazardous Waste, Pub. L. No. 94–580, Resource Conservation and Recovery Act Laws and Regulations (1976).

Plumbridge, W. J., & Gagg, C. R. (2000). *The mechanical properties of lead-containing and lead-free solders-meeting the environmental challenge*.

Ramos-Ruiz, A., Wilkening, J. V., Field, J. A., & Sierra-Alvarez, R. (2017). Leaching of cadmium and tellurium from cadmium telluride (CdTe) thin-film solar panels under simulated landfill conditions. *Journal of Hazardous Materials*, *336*, 57–64. https://doi.org/10.1016/j.jhazmat.2017.04.052

Researchers at NREL Find Fewer Failures of PV Panels and Different Degradation Modes in Systems Installed after 2000. (2017, April 10). National Renewable Energy Laboratory. https://www.nrel.gov/news/program/2017/failures-pv-panels-degradation.html

Samadi, A., Kim, Y., Lee, S. A., Kim, Y. J., & Esterhuizen, M. (2022). Review on the ecotoxicological impacts of plastic pollution on the freshwater invertebrate Daphnia. *Environmental Toxicology*, *37*(11), 2615–2638. https://doi.org/10.1002/TOX.23623

Sanborn, M. D., Abelsohn, A., Campbell, M., & Weir, E. (2002). Identifying and managing adverse environmental health effects: 3. Lead exposure. *CMAJ • MAY*, *14*(10).

Sarmah, P., Katsumi, T., Takai, A., Gathuka, L. W., & Yamawaki, A. (2024). Leaching behavior of inert waste landfills. *Waste Management*, *182*, 32–41. https://doi.org/10.1016/J.WASMAN.2024.04.012

S.C. Department of Health and Environmental Control. (n.d.). *How Landfills Work*. Retrieved July 1, 2024, from https://scdhec.gov/environment/land-and-waste-landfills/how-landfills-work

Sharma, H. B., Vanapalli, K. R., Barnwal, V. K., Dubey, B., & Bhattacharya, J. (2021). Evaluation of heavy metal leaching under simulated disposal conditions and formulation of strategies for handling solar panel waste. *Science of the Total Environment*, *780*. https://doi.org/10.1016/j.scitotenv.2021.146645

Sinha, P., Heath, G., Wade, A., & Komoto, K. (2019). *Human Health Risk Assessment Methods for PV Part 2: Breakage Risks*. https://iea-pvps.org/wp-content/uploads/2020/01/Task_12-Human_Health_Risk_Assessment_Methods_for_PV_part_2.pdf

Sinha, P., Trumbull, V. L., Kaczmar, S. W., & Johnson, K. A. (2014). *Evaluation of potential health and environmental impacts from end-of-life disposal of photovoltaics*.

Sinha, P., & Wade, A. (2015). Assessment of Leaching Tests for Evaluating Potential Environmental Impacts of PV Module Field Breakage. *IEEE Journal of Photovoltaics*, *5*(6), 1710–1714. https://doi.org/10.1109/JPHOTOV.2015.2479459

Snyder, R. G., Hsut, S. L., & Krimm, S. (1978). Vibrational spectra in the C-H stretching region and the structure of the polymethylene chain. *Spectrochimica Acta*, *34*, 395–406.

Song, S., He, C., Zhuo, Y., Yue, Y., & Shen, Y. (2023). How particle sizes affect silver leaching from c-Si photovoltaic solar cells: Insights from integrated experimental and numerical investigations. *Solar Energy Materials and Solar Cells*, *261*, 112520. https://doi.org/10.1016/J.SOLMAT.2023.112520

Spalvins, E., Dubey, B., & Townsend, T. (2008). Impact of electronic waste disposal on lead concentrations in landfill leachate. *Environmental Science and Technology*, *42*(19), 7452–7458. https://doi.org/10.1021/es8009277

Tamizhmani, G., Shaw, S., Libby, C., Patankar, A., & Bicer, B. (2019). Assessing Variability in Toxicity Testing of PV Modules. *Conference Record of the IEEE Photovoltaic Specialists Conference*, 2475–2481. https://doi.org/10.1109/PVSC40753.2019.8980781

Tammaro, M., Salluzzo, A., Rimauro, J., Schiavo, S., & Manzo, S. (2016). Experimental investigation to evaluate the potential environmental hazards of photovoltaic panels. *Journal of Hazardous Materials*, *306*, 395–405. https://doi.org/10.1016/J.JHAZMAT.2015.12.018

Technical Reference Document for Liquid Manure Storage Structures Compacted Clay Liners. (2007).

Tkaczyk, A., Bownik, A., Dudka, J., Kowal, K., & Ślaska, B. (2021). Daphnia magna model in the toxicity assessment of pharmaceuticals: A review. *Science of The Total Environment*, *763*, 143038. https://doi.org/10.1016/J.SCITOTENV.2020.143038

Tomasik, P., Magadza, C. H. D., Mhizha, S., & Chirume, A. (1995). The metal - Metal interactions in biological systems Part III. Daphnia magna. *Water, Air, & Soil Pollution*, *82*(3–4), 695–711. https://doi.org/10.1007/BF00479420/METRICS

Traudt, E. M., Ranville, J. F., & Meyer, J. S. (2017). Effect of age on acute toxicity of cadmium, copper, nickel, and zinc in individual-metal exposures to Daphnia magna neonates. *Environmental Toxicology and Chemistry*, *36*(1), 113–119. https://doi.org/10.1002/ETC.3507

Ucan-Marin, F. (2015). *A literature review on the aquatic toxicology of petroleum oil: An overview of oil properties and effects to aquatic biota*. http://www.dfo-mpo.gc.ca/csas-sccs/

United Nations. (2023). *Globally Harmonized System of Classification and Labelling of Chemicals (GHS)* (10th ed.). United Nations Economic Commission for Europe.

U.S. Energy Information Administration. (2024, June 12). *Form EIA-860 Detailed Data with Previous Form Data (EIA-860A/860B)*. Independent Statistics and Analysis. https://www.eia.gov/electricity/data/eia860/

U.S. Environmental Protection Agency. (n.d.). *National Recommended Water Quality Criteria - Aquatic Life Criteria Table*. Retrieved June 16, 2024, from https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table

U.S. Environmental Protection Agency. (1992). *Method 1311 Toxicity Characteristic Leaching Procedure*. https://www.epa.gov/sites/default/files/2015-12/documents/1311.pdf

U.S. Environmental Protection Agency. (1996). *Method 3050B Acid Digestion Of Sediments, Sludges, and Soils*. https://www.epa.gov/esam/epa-method-3050b-acid-digestion-sediments-sludges-and-soils

Vishnupriya, A., & Rajagopalan, V. (2022). Comparative Performance of Compacted Clay Liner (CCL) and Geosynthetic Clay Liner (GCL). *Issue 1 Journal of Bioanalytical Methods and Techniques Annex Publishers | Www.Annexpublishers.Com*, *2*(1), 103. www.annexpublishers.com

Vorobieva, O. V., Isakova, E. F., Zaec, M. A., Merzelikin, A. Y., & Samoilova, T. A. (2020). Toxicity of Aluminum Ions to Daphnia magna Straus Depending on the Hardness of Natural and Artificial Water. *Moscow University Biological Sciences Bulletin*, *75*(4), 231–236. https://doi.org/10.3103/S0096392520040124/FIGURES/1

Zapf-Gottwick, R., Koch, M., Fischer, K., & Hamann, L. (2015). *Leaching Hazardous Substances out of Photovoltaic Modules*. https://doi.org/10.15379/2408-977X.2015.02.02.2

Zhang, C., Jiang, J., Ma, E., Zhang, L., Bai, J., Wang, J., Bu, Y., Fan, G., & Wang, R. (2022). Recovery of silver from crystal silicon solar panels in Self-Synthesized choline Chloride-Urea solvents system. *Waste Management*, *150*, 280–289. https://doi.org/10.1016/J.WASMAN.2022.07.003